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## THE OXIDATION OF HYDROXY DERIVATIVES OF BENZALDEHYDE, ACETOPHENONE AND RELATED SUBSTANCES.

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The object of the following paper is to describe a new and somewhat remarkable reaction by which polyhydric phenols result from the oxidation, under certain conditions, of hydroxy derivatives of benzaldehyde and acetophenone.[1]

If *o*- or *p*-hydroxybenzaldehyde (1 mol.) is dissolved in normal aqueous caustic soda (1 mol.) and 2–3 per cent. hydrogen peroxide (1 mol.) is then added to the yellow solution of the sodium salt, a change in color is soon perceived. After a few seconds the solution becomes brownish-red and this change is accompanied by a considerable rise in temperature. On acidifying the solution it is found that practically no unchanged aldehyde remains and on extraction with solvents an almost theoretical yield of catechol or quinol is obtained. In the aqueous residue, formic acid is readily detected and if excess of hydrogen peroxide is employed, carbon dioxide resulting from the further oxidation of the formic acid is also formed. *No significant amount of hydroxybenzoic acid is formed in either case.*

[1] Cf. P. Chem. Soc., **1909.**

The net result of the reaction may be expressed as follows, but, as will appear later, the equation does not satisfactorily elucidate the change:

$$C_6H_4\begin{matrix}OH\\CHO\end{matrix} + H_2O_2 = C_6H_4(OH)_2 + HCOOH$$

*o*- and *p*-Hydroxyacetophenone behaved in similar fashion, yielding on oxidation catechol and quinol, respectively. A small but definite yield of quinol was also obtained by the oxidation of *p*-hydroxyphenylethyl ketone.

The same reaction was also found to occur in the case of the majority of halogen, hydroxy and nitro derivatives of *o*- and *p*-hydroxybenzaldehyde, as recorded in the following table. The products comprise several undescribed substituted polyhydric phenols and, as in many cases the yields are good, the reaction may prove to be of considerable value for the preparation of these substances, some of which are difficult to obtain by other methods.

On investigating the behavior of *m*-hydroxybenzaldehyde and its derivatives it was found that with a possible exception (4-methoxy-3-hydroxybenzaldehyde—isovanillin) no similar reaction took place, and no formation of resorcinol or its derivatives was ever observed.

*I.* o- *and* p-*Hydroxy Derivatives.*

| Substance oxidized. | Product. |
|---|---|
| 2-Hydroxybenzaldehyde | Catechol |
| 4-Hydroxybenzaldehyde | Quinol |
| 5-Chlor-2-hydroxybenzaldehyde | 4-Chlorcatechol |
| 3,5-Dichlor-2-hydroxybenzaldehyde | 3,5-Dichlorcatechol |
| 3,5-Dichlor-4-hydroxybenzaldehyde | 2,6-Dichlorquinol |
| 5-Brom-2-hydroxybenzaldehyde | 4-Bromcatechol |
| 3-Brom-4-hydroxybenzaldehyde | Bromquinol |
| 3,5-Dibrom-2-hydroxybenzaldehyde | 3,5-Dibromcatechol |
| 3,5-Dibrom-4-hydroxybenzaldehyde | 2,6-Dibromquinol |

| Substance oxidized. | Product. |
|---|---|
| 3,5-Diiod-4-hydroxybenzaldehyde | No appreciable phenol formation |
| 3-Nitro-2-hydroxybenzaldehyde | 3-Nitrocatechol |
| 5-Nitro-2-hydroxybenzaldehyde | 4-Nitrocatechol |
| 2-Nitro-4-hydroxybenzaldehyde | Nitroquinol* |
| 3-Nitro-4-hydroxybenzaldehyde | No appreciable phenol formation |
| 2,4-Dihydroxybenzaldehyde | Hydroxyquinol |
| 3,4-Dihydroxybenzaldehyde | Hydroxyquinol |
| 3-Methoxy-4-hydroxybenzaldehyde | 2-Methoxyquinol |
| 3-Methoxy-4-hydroxy-5-brombenzaldehyde | 2-Methoxy-6-bromquinol |
| 3-Methoxy-4-hydroxy-5-nitrobenzaldehyde | No appreciable phenol formation |
| 3-Methoxy-4-hydroxy-2-nitrobenzaldehyde | 3-Methoxy-2-nitroquinol |
| 2-Hydroxyacetophenone | Catechol |
| 4-Hydroxyacetophenone | Quinol |
| 2,4-Dihydroxyacetophenone | Hydroxyquinol |
| 2,5-Dihydroxyacetophenone | Hydroxyquinol* |
| 2-Hydroxy-4-methoxyacetophenone | Methoxyquinol* |
| 2-Hydroxy-4-ethoxyacetophenone | Ethoxyquinol* |
| 4-Hydroxyphenylethyl ketone. | Quinol. |

*II.* m-*Hydroxy Derivatives.*

| Substance oxidized. | Product. |
|---|---|
| 3-Hydroxybenzaldehyde | No phenol formation |
| Brom-3-hydroxybenzaldehyde | No phenol formation |
| 2-Nitro-3-hydroxybenzaldehyde | No phenol formation |
| 6-Nitro-3-hydroxybenzaldehyde | No phenol formation |
| 3-Hydroxy-4-methoxybenzaldehyde | Doubtful phenol formation |
| 3-Hydroxyacetophenone | No phenol formation. |

* The four substances marked with an asterisk (*) were not actually isolated in a pure state. Their formation was inferred from characteristic qualitative reactions.

The behavior upon oxidation of a large number of other halogen, nitro, amino and methoxy derivatives of benzaldehyde and acetophenone which did not contain a free hydroxyl group in the ortho or para position was also examined but in no case could any reaction be demonstrated analogous to the one under discussion.

From the preceding statements it is clear that under the conditions prevailing in these experiments, *only those derivatives of benzaldehyde and acetophenone will yield polyhydric phenols upon oxidation which already contain a free hydroxyl group in the ortho or para position.*

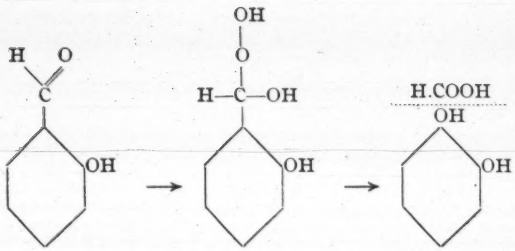
In the attempt to learn more of the conditions under which polyhydric phenols are formed by the oxidation of hydroxyaldehydes and ketones, a number of experiments were made in which oxidizing agents other than hydrogen peroxide were employed. In almost all of these experiments the sodium salt of *o*-hydroxybenzaldehyde was selected as the substance to be oxidized for the reasons that its conversion into catechol, at least when oxidized with hydrogen peroxide, takes place with especial ease, and in addition any catechol that may be formed is readily detected. It was found that sodium peroxide, barium peroxide, benzoylhydrogen peroxide ($C_6H_5.CO.O.OH$) and Caro's acid, in addition to hydrogen peroxide, were all capable of effecting the oxidation of *o*-hydroxybenzaldehyde with formation of catechol. On the other hand, the employment of lead peroxide, manganese peroxide, benzoyl superoxide ($C_6H_5.CO.O.O.CO.C_6H_5$), silver oxide, potassium permanganate, potassium bichromate, potassium ferricyanide, oxidation on prolonged exposure to the air, both in the presence and absence of benzaldehyde, and also oxidation in the animal organism in no case resulted in the formation of catechol, but in most cases salicylic acid was formed. The fact that oxidation of the sodium salt of *o*-hydroxybenzaldehyde, when exposed to the air, does not give catechol is perhaps somewhat surprising in view of the observations of Baeyer upon the mode of oxidation of benzaldehyde when exposed to the air. The formation of a superoxide, $C_6H_5.CO.O.OH$, as an initial product of the auto-oxidation of benzaldehyde would appear to be a reaction

which, if it occurred in the case of *o*-hydroxybenzaldehyde, might be expected to result in the formation of catechol. In relation to this reaction it is interesting to note the similar behavior of vanillin and other aldehydes which yield phenols on oxidation with hydrogen peroxide but which yield the corresponding acids when allowed to undergo spontaneous oxidation by prolonged free exposure to the air.

An observation which probably is of significance in any consideration of the mechanism of the oxidation of the sodium salt of salicylic aldehyde with superoxides is the apparent dependence of the reaction upon the presence of water. Neither the sodium salt of benzoyl hydrogen peroxide nor sodium peroxide can oxidize *o*-hydroxybenzaldehyde with formation of catechol if the reaction be carried out in dry ether. In the case of sodium peroxide a yellow salt is formed which may be decomposed with ice water without any catechol being formed. On boiling the salt with water, catechol and unchanged *o*-hydroxybenzaldehyde are obtained.

It is difficult to picture the mechanism of the conversion of an *o*- or *p*-hydroxybenzaldehyde into a dihydric phenol, but several possibilities present themselves as worthy of consideration.

The fact that thus far superoxides constitute the only class of oxidizing agents which have been found capable of bringing about the reaction suggests the possibility of an intermediate formation of a superoxide such as is formed, for example, by the combination of chloral and hydrogen peroxide ($CCl_3.CH(OH).O.OH$). The additive compound thus produced might conceivably undergo rearrangement, with formation of a phenol and formic acid. The oxidation of *o*-hydroxybenzaldehyde according to this view might be represented as follows:




There are, however, a number of objections to such an hypothesis, for it offers no explanation of the fact that apparently only hydroxy derivatives of benzaldehyde are capable of undergoing the transformation, nor of the differing behavior of the *m*- when contrasted with the *o*- and *p*-hydroxy derivatives.

The investigations of Hantzsch upon the relation between the color and constitution of salts of the hydroxybenzaldehydes have already indicated the probable existence of two series of salts: colorless phenolic salts of normal structure, *e. g.*, $C_6H_4(OMe).CHO$, and colored salts of quinoid structure, *e. g.*, $C_6H_4\langle{}^{O}_{CHOMe}$, and these observations appear to have a direct bearing upon the reaction under consideration.

If it be assumed that in aqueous solutions of the salts of the *o*- and *p*-hydroxy derivatives of benzaldehyde and acetophenone at least part of the substance is in the quinoid form, $C_6H_4\langle{}^{O}_{C(OMe)R}$ (or in the form of the ions resulting from the dissociation of the quinoid salt), and that the superoxides have the property of oxidizing this form but not the true phenolic salts, a number of experimental facts may be readily correlated.

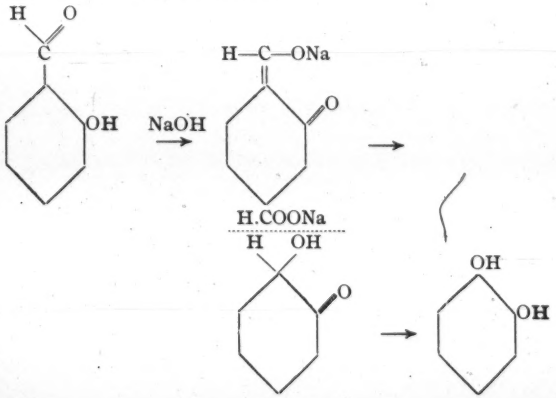
Such a theory indicates the reason why the substitution of an aldehyde grouping by an hydroxyl group upon oxidation with hydrogen peroxide only takes place when the aromatic

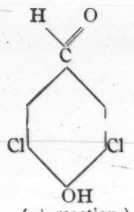
nucleus already contains at least one hydroxyl group in the *o*- or *p*-position. It can furthermore explain the reason of the inhibition of the transformation if the hydrogen atom of the hydroxyl group be replaced by an alkyl group, and in addition the nonreactivity of the *m*-hydroxy derivatives is intelligible. The difficulty of obtaining catechol by the oxidation of free *o*-hydroxybenzaldehyde may also reasonably be referred to absence of any large proportions of molecules of quinoid structure.

The fact that at least in the case of some superoxides the reaction takes place only in the presence of much water makes it appear possible that the reaction may be an ionic one.

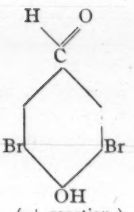
The difference in the products of the oxidation of the salts of *o*- and *p*-hydroxybenzaldehyde with superoxides on the one hand and other oxidizing agents, such as potassium permanganate, etc., on the other, may be referred to the possibility that of the two tautomeric forms in which the salts may be present in aqueous solution, the quinoid form is capable of oxidation by means of superoxides, whereas with the other oxidizing reagents, the salt reacts in the phenolic form.

The conversion of *o*-hydroxybenzaldehyde into catechol may be formulated as follows:

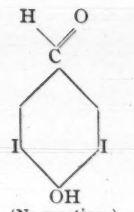




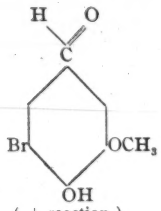
( + reaction.)



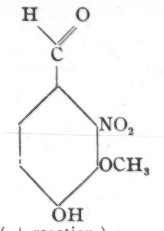
( + reaction.)



(No reaction.)



( + reaction.)



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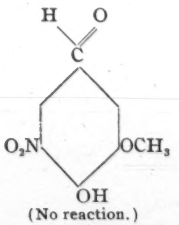
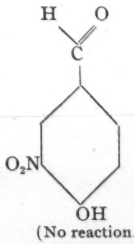


(No reaction.)



(No reaction.)

The table on p. 478 contains a few results which at first sight appear anomalous and require passing mention. Thus it was found that while 3,5-dichlor-4-hydroxybenzaldehyde and 3,5-dibrom-4-hydroxybenzaldehyde both gave substituted quinols upon oxidation, the corresponding 3,5-diiodo-4-hydroxybenzaldehyde did not react. A similar failure to react was shown in the case of 5-nitrovanillin and 5-nitro-4-hydroxy-

benzaldehyde, although the related 5-bromvanillin readily reacted, as did also 2-nitrovanillin. These results appear more clearly when tabulated as follows:

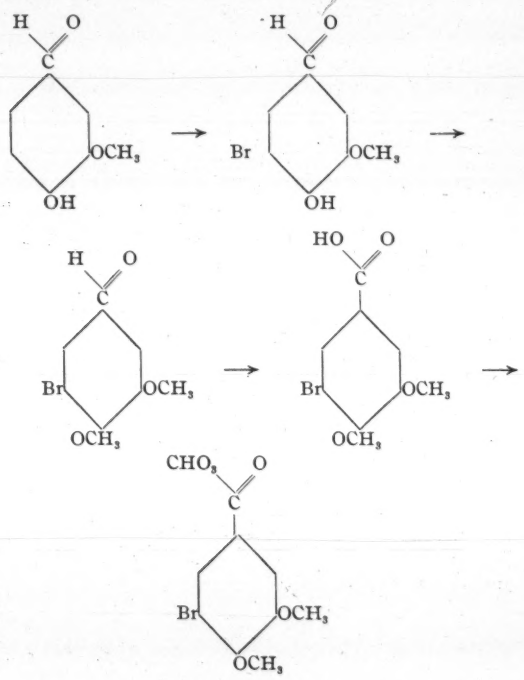
A consideration of the results shows that the cause of non-reactivity cannot be assigned singly to either the nature or position of the substituents but is to be sought in a combination of both factors. Hantzsch[1] has concluded from some observations upon the color of the salts of derivatives of *p*-hydroxybenzophenone that the presence of negative substituents adjacent to the hydroxyl group tends to inhibit the formation of quinoid salts, and hence the salts retain a phenolic structure. Such a view applied to the anomalous results just mentioned accords with the observed facts, but it is difficult to obtain direct evidence of its correctness, and moreover it is not clear why the 3,5-dichlor- and 3,5-dibrom-*p*-hydroxybenzaldehydes should be capable of conversion into the corresponding phenols without great difficulty while under the same conditions the corresponding 3,5-diiodo derivative is unattacked.

Incidentally in connection with the experiments recorded in this paper, a convenient method for the preparation of bromvanillin is described. The properties of the substance were more carefully studied than hitherto was the case and the position of the bromine atom was determined.

By methylation with dimethyl sulphate and potash, bromvanillin gave a bromveratric aldehyde (m. p. 65°–66°) differing from the 6-bromveratric aldehyde (m. p. 150°) obtained by Decker and Girard[2] from the oxidation of benzylbromisopapaverin with potassium permanganate. The bromine in bromvanillin may therefore be either in position 2 or 5. By oxidizing the bromveratric aldehyde to the corresponding acid and converting the latter into the methyl ester it was possible to decide between the two possible structures. 2-Bromveratric acid methyl ester melts at 46°, whereas the isomeric 5-brom derivative melts at 71°.[3] The product ob-

[1] Ber. d. chem. Ges., **39**, 3093 (1906).
[2] *Ibid.*, **37**, 3809.
[3] Zincke and Francke: Ann. Chem. (Liebig), **293**, 187.

tained from bromvanillin melted at 70°, from which it is inferred that the bromine atom in the former substance occupied position 5.




EXPERIMENTAL.

*Experiments on the Oxidation of Salicylic Aldehyde.*—The oxidation of salicylic aldehyde to catechol is effected at least as readily as any of the other analogous reactions; accordingly this substance was selected for making a large number of trial observations.

*Oxidation of Various Salts of Salicylic Aldehyde.*—It was found that the sodium, potassium and ammonium salts were all readily converted into catechol by treatment with hydrogen peroxide. These experiments were conducted by dissolving 0.01 gram molecule = 1.22 grams salicylic aldehyde in 10 cc. of normal alkali and adding a slight excess of hydrogen peroxide. The liquid becomes warm and somewhat dark. On acidifying, no precipitate of unchanged aldehyde is obtained. In an experiment in which the free aldehyde (1.22 grams) and hydrogen peroxide were mixed together previously, and then small additions of caustic soda were made with vigorous shaking during the intervals, it was found that 9.0 cc. were needed to produce a permanent alkalinity to litmus, while 10.5 were needed when phenolphthalein was employed as indicator. The theoretical amount for 1 molecule was 10.0 cc. The difference between the two determinations is doubtless due to the production of carbonates from the oxidation of the formic acid produced in the reaction.

The amount of hydrogen peroxide taking part in the reaction was determined by dissolving 0.01 gram molecule = 1.22 grams of salicylic aldehyde in 10 cc. N sodium hydroxide solution and adding definite amounts of hydrogen peroxide of known strength (1 cc. = 0.0137 gram oxygen). When an amount (12 cc.) equivalent to slightly more than 0.01 molecule oxygen (11.7 cc.) was added, no unchanged salicylic aldehyde was precipitated on acidification. When 9.0 cc. were employed there was slight precipitation and a large precipitation when 6.0 cc. were taken. From the preceding results it may be justly assumed that the reaction takes place in the proportion of 1 molecule of aldehyde, 1 molecule of alkali and 1 molecule hydrogen peroxide.[1]

It was found that while the formation of catechol from free salicylic aldehyde and hydrogen peroxide could be readily demonstrated when the two substances were boiled together, under a reflux condenser, the reaction was slow and did not take place with the smoothness characteristic of the oxidation

[1] In the oxidation of nitro derivatives of *o*- and *p*-hydroxybenzaldehyde it is advisable to use at least 2 molecules of alkali.

of the salts. That this difference was not simply due to the sparing solubility of the free aldehyde was proved by carrying out similar experiments in acetone and in alcoholic solution. When the materials were allowed to stand at room temperature even for many hours no formation of catechol was detected.

*Preparation of Catechol from Salicylic Aldehyde.*—An almost theoretical yield of catechol may be obtained from salicylic aldehyde by adopting the following method which is typical of all the experiments subsequently made in which other aldehydes were oxidized.

Salicylic aldehyde (1 mol.) is dissolved in normal caustic soda solution (1 mol.) and dilute hydrogen peroxide (2.5–3 per cent.) equivalent to 1.25 molecules added in one portion. The liquid changes in color from yellow to light brown and soon becomes hot. The mixture is allowed to stand until cool and is then acidified with a little sulphuric acid and sodium bicarbonate is added in slight excess. The liquid is then extracted with ether. On evaporation of the ether a crystalline residue of catechol remains behind which is readily purified by a single recrystallization from benzene. The substance melted at 104° and was identical in every respect with catechol of other origin. Analysis:

| | Calculated for $C_6H_6O_2$. | Found. |
|---|---|---|
| C | 65.28 | 65.45 |
| H | 5.51 | 5.45 |

*5-Chlor-2-hydroxybenzaldehyde.*—This substance was prepared according to Biltz and Stepf's[1] directions by the limited chlorination of salicylic aldehyde. On oxidation of the sodium salt, chlorcatechol was obtained in good yield.

*3,5-Dichlor-2-hydroxybenzaldehyde.*—The prolonged chlorination of salicylic aldehyde dissolved in glacial acetic acid gave a good yield of dichlorsalicylic aldehyde. The substance melted at 95°–96° and crystallized from slightly diluted acetic acid in large prisms which retain a very faint yellow color. These

[1] Ber. d. chem. Ges., **37**, 4022.

observations accord with those of Biltz and Stepf and are not in agreement with the results of earlier investigators.

On oxidation an excellent yield of 3,5-dichlorcatechol was obtained. The substance is only moderately soluble in cold water; very soluble in hot water. It crystallizes in long, flat, colorless prisms, melting sharply at 83°–84°. Its aqueous solutions instantly reduce ammoniacal silver nitrate and give with ferric chloride a clear green coloration which becomes violet on addition of sodium bicarbonate. Analysis:

| | |
|---|---|
| 0.2270 gram gave 0.3610 gram AgCl = | 39.28 per cent. Cl |
| $C_6H_4O_2Cl_2$ requires | 39.14 per cent. Cl |

*5-Brom-2-hydroxybenzaldehyde.*—This substance was prepared by the bromination of salicylic aldehyde in glacial acetic acid solution. On oxidation it gave a substance exhibiting all the characteristics of a catechol derivative. The substance crystallizes from boiling petroleum, in which it is only slightly soluble, in thick prisms melting at 86°–87°. It is much more soluble in benzene and very soluble in water and alcohol. Its aqueous solutions instantly reduce ammoniacal silver nitrate in the cold and give a clear green coloration with ferric chloride, turning violet on addition of sodium bicarbonate. Analysis:

| | |
|---|---|
| 0.1052 gram gave 0.1042 gram AgBr = | 42.15 per cent. Br |
| $C_6H_5O_2Br$ requires | 42.32 per cent. Br |

*3,5-Dibrom-2-hydroxybenzaldehyde.*—Salicylic aldehyde was brominated in acetic acid solution with rather more than 2 molecules of bromine. The recrystallized aldehyde melted at 83°–85° and on oxidation readily gave a catechol derivative, although a not inconsiderable amount of unoxidized aldehyde remained. The ethereal extract from the acidified and filtered solution was evaporated to dryness and then stirred with a little cold water and filtered from a small insoluble residue. The filtrate on concentration slowly crystallized, but the melting point of the crystals was not sharp. It was found difficult to recrystallize the substance, which, however, readily gave the characteristic reaction for a catechol derivative;

accordingly it was treated with an excess of bromine and thus converted into the beautifully crystalline tetrabromcatechol, melting at 189°, already described by Hlasiwetz.[1]

*3-Nitro-2-hydroxybenzaldehyde.*—The sodium salt of this substance (1 mol.) was mixed with hydrogen peroxide (1.5 mols.) and normal caustic soda was added by degrees until the solution acquired a permanent purple color. On acidifying the solution a considerable amount of unchanged aldehyde was precipitated. 3-Nitrocatechol was obtained by extracting the filtrate with ether and recrystallizing from water containing a little alcohol.

*5-Nitro-2-hydroxybenzaldehyde.*—This substance was oxidized in the same manner as in the preceding case but the yield of 5-nitrocatechol was materially better (about 70 per cent.). The substance was crystallized from a very little water, in which it is very soluble, and melted at 174°. This result differs but slightly from the observations of Bamberger and Czerki (175°.5) and is materially higher than the melting points recorded by Benedikt and other observers.[3]

p-*Hydroxybenzaldehyde.*—The salts of this substance upon oxidation with hydrogen peroxide exhibited precisely the same phenomena as those observed in the case of salicylic aldehyde and the reaction was carried out in the same manner as in the case of the latter substance. The yield o' quinol approximated the theoretical amount. It was purified by crystallization from benzene or from water. The substance melted sharply at 170°. Analysis:

| | Calculated for $C_6H_6O_2$. | Found. |
|---|---|---|
| C | 65.40 | 65.45 |
| H | 5.61 | 5.45 |

Molecular weight by freezing point method, acetic acid for solvent:

Found, 114.3; calculated, 110.

*3,5-Dichlor-4-hydroxybenzaldehyde.*—*p*-Hydroxybenzaldehyde was chlorinated in glacial acetic acid according to the direc-

[1] Ann. Chem. (Liebig), **142**, 251.
[2] J. prakt. Chem., [2] **68**, 480.
[3] Ber. d. chem. Ges., **11**, 362; Mameli, Atti. R. Accad. Lincei, [5] **14**, II, 510.

tions of Auwers and Reis[1] and the product purified by crystallization from alcohol. The oxidation of the potassium salt with hydrogen peroxide took place smoothly with an excellent yield of 2,6-dichlorquinol. Crystallized from benzene or water, the substance was obtained in the form of needles melting at 163°–164°, agreeing with Kehrmann and Tiesler's observations.[2] On warming the substance with ferric chloride solution, 2,6-dichlorquinone, melting at 120°, was obtained.

*3- Nitro - 4 - hydroxybenzaldehyde.* — *p*-Hydroxybenzaldehyde was nitrated in glacial acetic acid with slightly more than the theoretical amount of concentrated nitric acid according to Paal's method.[3] The crude nitro derivative was purified by crystallization from alcohol. It was found that the salts of this substance were practically unattacked on treatment with hydrogen peroxide either in the cold or at the boiling temperature. The use of Caro's acid proved no more successful.

*3 - Brom - 4 - hydroxybenzaldehyde.*— *p*-Hydroxybenzaldehyde was brominated in chloroform solution according to Paal's method[4] and the product crystallized from boiling water. The sodium salt was readily oxidized with hydrogen peroxide, giving a good yield (60–70 per cent.) of bromquinol. The crude product melted at 110° but on recrystallization from a mixture of benzene and ligroin, the melting point rose to 113°–115°. Saraw[5] gives 110°–111° as the melting point of this substance.

*3,5-Dibrom-4-hydroxybenzaldehyde.*—This aldehyde was obtained according to Paal's[6] directions and crystallized in long needles melting at 180°–181°. It was found advisable to use 2 molecules of caustic soda, in place of 1 molecule, for the oxidation of this substance with hydrogen peroxide. The reaction took place readily, with the usual color and temperature changes. At the close of the reaction, on acidifying the solution, a precipitate consisting of a mixture of unchanged

[1] Ber. d. chem. Ges., **29,** 2356.
[2] J. prakt. Chem., [2] **40,** 481.
[3] Ber. d. chem. Ges., **28,** 2413.
[4] *Ibid.*, p. 2409.
[5] Ann. Chem. (Liebig), **209,** 105.
[6] *Loc. cit.*, p. 2410.

aldehyde and dibromquinol was obtained. The filtrate on extraction with ether gave a small yield of dibromquinol which crystallized from water in well-formed platelets melting at 163°–164°. The substance was doubtless identical with the 2,6-dibromquinol obtained by Ling[1] by the reduction of dibromquinone with sulphurous acid.

*3,5-Diiod-4-hydroxybenzaldehyde.*—This substance was prepared by the action of iodine and iodic acid upon *p*-hydroxybenzaldehyde.[2] No appreciable amount of diiodoquinol was obtained on treatment of its sodium salt with hydrogen peroxide.

*2,4-Dihydroxybenzaldehyde.*—One molecular proportion of caustic soda was used for the oxidation of this substance. The reaction with hydrogen peroxide was fairly vigorous but a considerable amount of aldehyde remained unoxidized and was removed by extracting the acidified solution with chloroform. On shaking with ether an extract was obtained which readily gave the reactions for hydroxyquinol, but the product was not pure. It was further identified by conversion into tribromhydroxyquinol by means of bromine. The product was crystallized from alcohol and from chloroform and melted at 206°–207°, in agreement with the observations of Barth and Schroeder.[3]

*3,4-Dihydroxybenzaldehyde.*—On oxidation of the monopotassium salt of this aldehyde with hydrogen peroxide the substance behaved in precisely the same manner as the preceding substance, a small quantity of hydroxyquinol being obtained.

*Vanillin.*—An almost theoretical yield of the methyl ether of hydroxyhydroquinone was obtained by the oxidation of the sodium salt of vanillin with hydrogen peroxide. The substance was crystallized from benzene and melted at 82°–83°. This substance was previously obtained by Will[4] by the reduction of the methyl ether of 2-hydroxyquinone with sulphurous acid.

*5-Nitrovanillin.*—As in the case of the similarly constituted

[1] Trans. Chem. Soc., **61**, 562.
[2] Ber. d. chem. Ges., **28**, 2412.
[3] Monats. Chem., **5**, 593.
[4] Ber. d. chem. Ges., **21**, 606.

*m*-nitro-*p*-hydroxybenzaldehyde, no formation of a quinol derivative could be detected upon oxidizing this substance with hydrogen peroxide.

*2-Nitrovanillin.*—This substance was prepared according to the method of Pschorr and Sumuleanu[1] by the nitration of acetylvanillin and saponification of the resulting nitro derivatives with caustic soda. The product was crystallized from boiling water and melted at 135°. On oxidation of the potassium salt with hydrogen peroxide (1.5 mols.) and caustic potash (2 mols.) an excellent yield of 2-nitro-3-methoxyquinol was obtained. The substance crystallizes from benzene in large deep-red prisms melting at 86°.5–87°.5. Analysis:

0.2555 gram gave 0.01904 gram N = 7.45 per cent. N
$C_7H_7O_5N$ requires 7.57 per cent. N

*5-Bromvanillin.*—A bromvanillin was obtained by Carles and by Tiemann and Haarmann[2] by the bromination of aqueous or alcoholic solutions of vanillin and is described as a yellowish substance melting at 160°–161°, sparingly soluble in cold water. The constitution of the substance was not determined. It was found that bromination in aqueous solution, even with the addition of potassium acetate, was very undesirable owing to the formation of deeply pigmented impurities. The following conditions were found advantageous for the preparation of bromvanillin.

Vanillin (15.2 grams) is dissolved in warm glacial acetic acid (30 cc.) and to the solution, while cooled under the tap, bromine (5.4 cc.) dissolved in acetic acid (20 cc.) is added fairly rapidly with shaking. Crystallization occurs almost immediately and water is then added and the crystals are filtered off and crystallized from boiling 95 per cent. alcohol. Bromvanillin separates in large cubic crystals which when freshly recrystallized are perfectly colorless but acquire a slight yellowish tinge on standing. The yield of recrystallized substance is 20–21 grams. The substance melts at 163°–164° and is sparingly soluble in cold but readily in hot alcohol. It is practically insoluble in hot or cold water, sparingly soluble

[1] Ber. d. chem. Ges., **32**, 3408.
[2] *Ibid.*, **7**, 614.

in ether or benzene. Bromvanillin dissolves in aqueous caustic potash to give a light yellowish solution of the potassium salt. Bromvanillin was methylated in the usual manner by warming the substance with a considerable excess of dimethyl sulphate and a 10 per cent. solution of caustic potash. The product, 5-bromveratric aldehyde, separates in the form of an oil, insoluble in alkali, which quickly becomes solid on cooling. It is readily recrystallized from 80 per cent. alcohol and separates in the form of white masses of felted needles which melt sharply at 65°–66°.

5-Bromveratric aldehyde was oxidized by boiling the substance for about one hour with slightly more than the theoretical amount of chromic acid dissolved in 5 parts of glacial acetic acid. On dilution with water, the precipitated acid was filtered off and dried and then boiled with petroleum ether to remove any unchanged aldehyde. The 5-bromveratric acid remaining was crystallized from dilute alcohol and then converted into the methyl ester by means of methyl alcohol and hydrochloric acid in the usual way. The product, after crystallization from petroleum, melted sharply at 69°–70° and was identical with the 5-bromveratric acid methyl ester prepared by Zincke and Franke.[1]

5-Bromvanillin (4.6 grams) was converted into the potassium salt by warming with 21 cc. N caustic potash solution and then adding a 30 per cent. excess of dilute hydrogen peroxide. The liquid at once became dark purple and heat was evolved. After gently warming for a few minutes, the products of the reaction were isolated in the usual way. The ether extract gave slightly more than 2.0 grams of a pigmented crystalline residue, which after crystallization from boiling water gave a good yield of pure substance. There can be little doubt that the compound is 5-brom-3-methoxyquinol. The substance is colorless when pure and crystallizes from water in thick prisms or needles, melting at 141°–143°. It is only moderately soluble in cold water, easily in hot, easily soluble in hot benzene, almost insoluble in petroleum. The aqueous solution reduces

[1] Ann. Chem. (Liebig), **293**, 183.

alkaline silver solutions and Fehling's solution in the cold. Analysis:

0.2426 gram gave 0.2062 gram AgBr = 36.2 per cent. Br
$C_7H_7O_3Br$ requires 36.5 per cent. Br

*The Oxidation of Derivatives of Acetophenone.*

The following ketones were oxidized by warming their ammonium or sodium salts with a 25 per cent. excess above the theoretical amount (1 mol.) of hydrogen peroxide. The reaction does not take place as easily as in the case of the corresponding aldehydes and the yields, particularly in the case of the dihydroxyketones, are smaller.

*Oxidation of* p-*Hydroxyacetophenone.*—The ketone was gently boiled for a few minutes with a slight excess of ammonia and hydrogen peroxide. The sodium salt was also used successfully. On acidifying and allowing to stand, a considerable amount of unchanged ketone crystallized out. The filtrate was extracted with ether and the crude quinol recrystallized from benzene. It melted at 170°. Yield, 40–50 per cent. Analysis:

| | Calculated for $C_6H_6O_2$. | Found. |
|---|---|---|
| C | 65.34 | 65.45 |
| H | 5.56 | 5.45 |

o-*Hydroxyacetophenone.*—This substance was prepared by reducing *o*-nitroacetophenone, separated according to Camp's[1] directions from the products of nitration of acetophenone, and subsequently heating the solution of the diazotized base. The amount of pure substance obtained was small, but it was easy to identify catechol as a product of the oxidation of its sodium salt with hydrogen peroxide by proceeding in the same manner as in the case of the preceding para derivative.

*2,4-Dihydroxyacetophenone* (*Resacetophenone*).—The sodium salt of this substance was oxidized in the usual way, the solution being heated slowly to the boiling point, but much un-

[1] Archiv. Pharm., **240**, 1 (1902).

changed ketone was precipitated on acidification. On extraction with ether and treatment of the ethereal residue with a little cold water, a solution was obtained which gave the characteristic reactions for hydroxyhydroquinone. Ferric chloride gave an olive-greenish coloration, becoming blue on addition of a trace of sodium carbonate and wine-red when an excess of the latter salt was added. The yield of hydroxyhydroquinone was very poor. On treatment with bromine, as in the case of the product from 2,4-dihydroxybenzaldehyde, tribromhydroxyhydroquinone was obtained.

*Monomethyl and Monoethyl Ethers of 2,4-Dihydroxyacetophenone.*—Qualitative experiments with the sodium salts of these substances showed that both of them were oxidized by hydrogen peroxide, with formation of small quantities of hydroxyhydroquinone methyl and ethyl ether, respectively

*2,5-Dihydroxyacetophenone.*—The behavior of the sodium salt of this substance on oxidation with hydrogen peroxide was similar to that of 2,4-dihydroxyacetophenone. Much unchanged substance, together with a little hydroxyquinol, were obtained.

*The Oxidation of* p-*Hydroxyphenylethyl Ketone.*

This ketone was obtained in small yield by the condensation of phenol and propionic acid by means of zinc chloride according to the directions of Goldzweig and Kaiser.[1] The product was repeatedly recrystallized from water and melted sharply at 148°–149°. The potassium salt was oxidized in the usual way by dissolving 0.01 gram molecule of the substance (= 1.50 grams) in 10 cc. of normal potash solution and adding about 0.02 gram molecule of hydrogen peroxide. No appreciable action took place in the cold, so the mixture was gently boiled for about fifteen minutes. The liquid was then acidified and allowed to stand overnight so as to make the precipitation of unchanged ketone as complete as possible. The filtrate on extraction with ether gave a minute quantity of quinol (0.15 gram). It was characterized by its melting point (169°) and the usual reactions.

[1] J. prakt. Chem., [2] **53**, 86.

*Oxidation of Derivatives of* m-*Hydroxybenzoic Acid.*

The oxidation with hydrogen peroxide of the salts of the halogen and nitro derivatives of *m*-hydroxybenzoic acid, referred to in the table on p. 479, gave uniformly negative results. The only derivative of *m*-hydroxybenzaldehyde which gave any trace of a resorcin derivative was 3-hydroxy-4-methoxybenzaldehyde (isovanillin). This substance, prepared by the action of methyl iodide upon the monopotassium salt of protocatechuic aldehyde, was converted into the potassium salt and then heated with excess (2 mols.) of hydrogen peroxide. No appreciable action took place in the cold, so the solution was gently boiled. On acidifying and allowing the solution to stand, much dark colored unchanged substance was precipitated. On extracting the filtrate with ether, after neutralizing with sodium bicarbonate, a very small quantity of crystalline substance was obtained which gave certain reactions which indicated the possibility of the presence of a polyhydric phenol. The quantity was too small to satisfactorily purify but the following facts were ascertained: The substance was very soluble in water, alcohol and ether, but insoluble in petroleum ether. The aqueous solutions gave a deep violet red coloration with ferric chloride and reduced ammoniacal silver nitrate and Fehling's solution in the cold.

*Oxidation of* o-*Hydroxybenzaldehyde with Various Reagents.*

Sodium and barium peroxides were both found to bring about the formation of catechol from salicylic aldehyde. In the case of sodium peroxide, the powdered substance (1.5 mols.) was added in small portions to an ice-cooled mixture of salicylic aldehyde (1 mol.) with ten parts of water. The substance was subsequently warmed to 60°. On acidifying and extracting with ether, catechol was obtained in large quantity. The reaction in the case of barium peroxide was effected by heating the mixture of peroxide, aldehyde and water under a reflux condenser. A similar method was adopted in the case of the peroxide of manganese and lead but with these reagents no catechol was formed.

Benzoylhydrogen peroxide was prepared by Baeyer's method by the action of sodium ethylate (1 mol.) on benzoyl superoxide (1 mol.) in ethereal solution. The white precipitate of the sodium derivative of benzoylhydrogen peroxide was dissolved in water and the solution so obtained added directly to a solution of the sodium salt of salicylic aldehyde. The solution at once became darker and heat was evolved. On acidifying, a large precipitate of benzoic acid was obtained which melted at 121° after recrystallization from water. The filtrate, on extraction with ether, gave an abundant yield of catechol. Neither benzoylcatechol nor benzoylformic acid could be detected.

The action of Caro's acid upon salicylic aldehyde was investigated under precisely the same conditions as those adopted by Baeyer and Villiger in the preparation of the superoxide of benzaldehyde.[1] No superoxide of salicylic aldehyde could be isolated, but on dilution and extraction with ether catechol was obtained.

LABORATORY OF DR. C. A. HERTER,
NEW YORK.

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[Contributions from the Sheffield Laboratory of Yale University.]

## CLXXIV.—RESEARCHES ON HALOGENAMINO ACIDS: IODINE DERIVATIVES OF ORTHOTOLUIDINE. THE 3-IODAMINOBENZOIC ACIDS.[2]

### [SEVENTH PAPER.]

BY HENRY L. WHEELER AND LEONARD M. LIDDLE.

Iodine acting on *p*-toluidine has been shown by us to yield two iodtoluidines, 1-methyl-3-iod-4-aminobenzene and 1-methyl-3,5-diiod-4-aminobenzene.

We now find that when iodine is mixed with *o*-toluidine only one iodine derivative is formed and this mono derivative can be melted with iodine without further substitution taking place. There is therefore considerable difference in the capacity

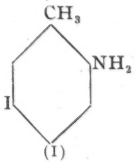
[1] Ber. d. chem. Ges., **33**, 2479.

[2] Part of a thesis presented by Leonard M. Liddle for the degree of Ph.D., Yale, 1909.

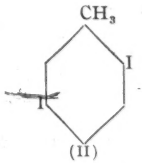
of these toluidines to take up iodine. A still greater tendency to take up iodine is shown in the case of *m*-toluidine. The compounds derived from this base will be described in a later paper.

The monoiod-*o*-toluidine, which is obtained smoothly and in excellent yield by mixing *o*-toluidine with iodine, proves to be 1-methyl-2-amino-5-iodbenzene (I). This substance has previously been prepared by Artmann[1] by an indirect method.

From this iod-*o*-toluidine we have prepared the new 2,5- or 3,6-diiodtoluene (II) by diazotizing and treating the solution with potassium iodide. We then found that this diiodtoluene is not identical with that prepared from diiod-*p*-toluidine.

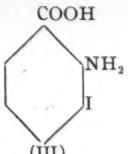


(I)



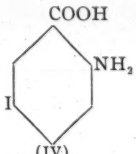
(II)

Grothe[2] obtained three of the four theoretically possible mononitro derivatives of *m*-iodbenzoic acid by nitrating the acid. Two of these acids, his so-called $\alpha$ and $\beta$ acids, he obtained in sufficient quantity to reduce to the corresponding iodamino acids. Both of these, he found, gave on further reduction *o*-aminobenzoic acid. One of these acids is therefore 2-amino-3-iodbenzoic acid (III) and the other must be 2-amino-5-iodbenzoic acid (IV). The question as to which is which was not decided.



(III)

$\alpha$ acid, m. p. 137°.



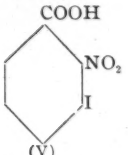
(IV)

$\beta$ acid, m. p. 209°.

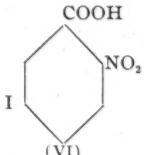
[1] Monats. Chem., **26**, 1097 (1905).
[2] J. prakt. Chem., [2] **18**, 326 (1878).

We have found that when the acetyl derivative of 1-methyl-2-amino-5-iodbenzoic (I) from *o*-toluidine and iodine is oxidized with potassium permanganate and the product boiled with concentrated hydrochloric acid a good yield of 2-amino-5-iodbenzoic acid (IV) results. This acid melting at 209° proved to be identical with Grothe's $\beta$-iod-2-aminobenzoic acid.

It follows from this that his $\alpha$-iodaminobenzoic acid, melting at 137°, is 3-iod-2-aminobenzoic acid (III). His $\alpha$-nitro-iodbenzoic acid, melting at 235°, is 2-nitro-3-iodbenzoic acid (V) and his $\beta$-nitroiodbenzoic acid, melting at 174°, is 2-nitro-5-iodbenzoic acid (VI).

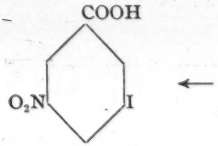



(V)
$\alpha$ acid, m. p. 235°.

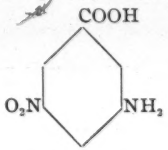



(VI)
$\beta$ acid, m. p. 174°.

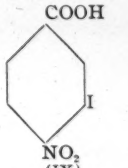
In Beilstein's *Handbuch*[1] Grothe's $\gamma$-nitroiodbenzoic acid, melting at 192°, is listed as 3-iod-5-nitrobenzoic acid (VII) but like his other acids it is represented as subject to interrogation. We have prepared this 3-iod-5-nitrobenzoic acid from Hübner's[2] 3-amino-5-nitrobenzoic acid (VIII) by means of the diazo reaction. An iodnitrobenzoic acid, melting at 167°, was obtained which is not identical with the acid described by Grothe. Since this completes the list of the theoretically possible mononitro acids derived from *m*-iodbenzoic, Grothe's $\gamma$ acid must be 3-iod-4-nitrobenzoic acid (IX).




(VII)
M. p. 167°.




(VIII)



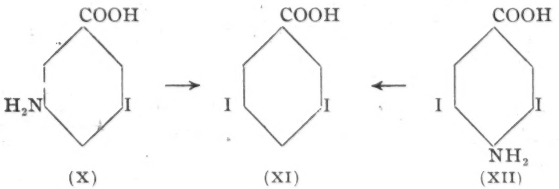

(IX)
$\gamma$ acid, m. p. 192°.

[1] [3] **2**, 1244.

[2] Ann. Chem. (Liebig), **222**, 81 (1884).

We have prepared 3-iod-5-aminobenzoic acid (X) by reducing 3-iod-5-nitrobenzoic acid. This completes the list of the four theoretically possible monaminobenzoic acids having an iodine atom in the meta position to the carboxyl group.

The diazotization of our 3-iod-5-aminobenzoic acid and subsequent treatment with potassium iodide gave 3,5-diiodbenzoic acid (XI), which proved to be identical with the acid obtained from Michael and Norton's[1] diiod-*p*-aminobenzoic acid (XII) on removing the amino group. This affords conclusive proof that the iodine atoms are in the 3,5-position in these compounds.




(X) (XI) (XII)

EXPERIMENTAL PART.

*5-Iod-2-aminotoluene.*—When *o*-toluidine and iodine, in molecular proportions, were mixed, heat was evolved and immediate substitution took place. In order to complete the reaction some ether, calcium carbonate, and a little water were added. The mixture was then warmed on the steam bath for a half hour, or until the iodine disappeared, the flask being attached to a return condenser. If the product was shaken out with ether and the ether evaporated the yield of crude product was over 90 per cent. of the theoretical, but the material was very dark. It was found that by distilling with steam a much better purification was effected. This removed all color and gave over 80 per cent. of the calculated amount of pure white solid. It is easily volatile in steam and it crystallizes in beautiful, large, colorless prisms from gasoline. It

[1] THIS JOURNAL, **1**, 264 (1879).

melted at 90°–91°. Artmann gives 91°–92°. In all other respects our product agreed with Artmann's descriptions.

| | Calculated for $C_7H_8NI$. | Found. |
|---|---|---|
| N | 6.01 | 5.83 |

*2,5-Diiodtoluene.*—Nineteen grams of 5-iod-2-aminotoluene, 100 cc. of concentrated hydrochloric acid, and 300 cc. of water were mixed and diazotized in the cold with 8 grams of sodium nitrite in 40 cc. of water. The clear, filtered solution was treated with about 38 grams of potassium iodide in 75 cc. of water. This produced a bulky precipitate, which was allowed to stand and then warmed until nitrogen was evolved and the substance sank down to a black oil. The free iodine was removed with a little sodium bisulphite and the oil was extracted with ether and distilled in steam. It came over easily and solidified on standing. When washed with a little ether and pressed on paper it melted at 30°–31°. It was very soluble in petroleum ether, ether, and hot alcohol but insoluble in water. When crystallized from strong alcohol, it gave long, colorless plates, which melted as before at 30°–31°.

| | Calculated for $C_7H_6I_2$. | Found. |
|---|---|---|
| I | 73.83 | 73.86 |

The melting point of this diiodtoluene is near that of 2,3-diiodtoluene (31°–32°). It differs notably from this compound in its volatility in steam, and when the substances were mixed the mixture immediately liquefied. The same result was produced on mixing with 3,5-diiodtoluene.

*5-Iod-2-acettoluide*, from 5-iod-2-aminotoluene and acetic anhydride, was difficultly soluble in water and separated in the form of fine needles. It is easily soluble in alcohol; from dilute alcohol it gave long, colorless needles melting to a clear oil at 169°.

| | Calculated for $C_9H_{10}ONI$. | Found. |
|---|---|---|
| N | 5.09 | 5.10 |

*5-Iod-2-benztoluide*, from the base and thiobenzoic acid, crystallized from alcohol in colorless needles, which melted to a clear oil at 184°. The material was insoluble in water.

| | Calculated for $C_{14}H_{12}ONI$. | Found. |
|---|---|---|
| N | 4.15 | 4.20 |

*5-Iod-2-acetaminobenzoic Acid.*—Six grams of 5-iod-2-acettoluide were suspended in 250 cc. of hot water which contained 12 grams of magnesium sulphate. Steam was forced in while 10.5 grams of potassium permanganate in 1 per cent. solution were slowly added during the course of 12 hours. The excess was then reduced with alcohol and the manganese dioxide was filtered off. The filtrate was evaporated to about 150 cc. and cooled. Some unaltered 5-iod-2-acettoluide (2.5 grams) separated. When the filtrate from this was made acid with hydrochloric acid a flocculent precipitate was formed which weighed 3.15 grams, or 47 per cent. of the calculated. The acid formed hairlike needles from water, in which it was difficultly soluble. Alcohol and alkali dissolved it very easily. When crystallized from 50 per cent. alcohol it formed burrs of colorless needles which melted with decomposition and effervescence at 235°.

| | Calculated for $C_9H_8O_3NI$. | Found. |
|---|---|---|
| N | 4.59 | 4.58 |

*5-Iod-2-aminobenzoic Acid.*—Grothe's β-iod-2-aminobenzoic acid was easily obtained when the above acetamino acid was warmed with hydrochloric acid. When the acid had dissolved, the solution was evaporated to dryness and the residue was taken up in ammonia and precipitated by acetic acid. The precipitate formed twinned prisms from dilute alcohol and melted at 209°–210°.

| | Calculated for $C_7H_6O_2NI$. | Found. |
|---|---|---|
| N | 5.32 | 5.39 |

*3-Iod-5-nitrobenzoic Acid.*—Hübner's 3,5-dinitrobenzoic acid[1] was reduced, according to his directions, to 3-amino-5-nitrobenzoic acid. Sixteen grams of this acid were dissolved in 100 grams of concentrated hydrochloric acid and 250 cc. of water. This solution was diazotized at 0° with 7.2 grams of

[1] *Loc. cit.*

sodium nitrite in 35 cc. of water, and then 55 grams of potassium iodide in 80 cc. of water were added. The mixture stood overnight and then was warmed. It was finally cooled in ice water and the crude acid which separated was found to weigh 18.1 grams, or 70 per cent. of the calculated. In another experiment 4 grams of nitramino acid gave 4.7 grams of iodnitro acid, 73 per cent. of the calculated. 3-Iod-5-nitrobenzoic acid dissolves in ammonia and is precipitated by acetic acid. It is not soluble in an excess of hydrochloric acid. It is readily soluble in alcohol and separates slowly in bunches of needles. It is difficultly soluble in cold water and only moderately soluble in hot, from which it crystallizes in long, slender needles. It has a straw-yellow color and melts to a yellow oil at 167°.

| | Calculated for $C_7H_4O_4NI$. | Found. I. | Found. II. |
|---|---|---|---|
| N | 4.77 | 4.77 | 4.85 |

This acid has the peculiar property of melting under hot water when a few drops of alcohol are added. Its melting point, color, and its lack of solubility in water show that it is not Grothe's γ-nitro-*m*-iodbenzoic acid.

*3-Iod-5-aminobenzoic Acid.*—Eight grams of 3-iod-5-nitrobenzoic acid were dissolved in 100 cc. of concentrated ammonia and added to a solution of 49 grams of ferrous sulphate in 200 cc. of warm water. The flask was closed with a tube provided with a water trap and heated on the steam bath for four and one-half hours. The mixture was then filtered and a small portion of the filtrate was precipitated with hydrochloric acid. The precipitate which was formed dissolved immediately in an excess of acid. The reduction was therefore complete. The main portion was evaporated to a small volume and then precipitated with acetic acid. This gave a finely divided precipitate which weighed 6.2 grams, or 87 per cent. of the calculated. It crystallized in long, straw-yellow spikes from dilute alcohol and melted to a clear oil at 197°.

| | Calculated for $C_7H_6O_2NI$. | Found. |
|---|---|---|
| N | 5.32 | 5.42 |

This acid gives a difficultly soluble hydrochloride. It is soluble in acetic acid.

*3,5-Diiodbenzoic Acid.*—Five grams of 3-iod-5-aminobenzoic acid were suspended in 50 cc. of concentrated hydrochloric acid and 150 cc. of water. Very little dissolved but the whole was placed in a freezing mixture and treated with 2 grams of sodium nitrite in 14 cc. of water. The precipitate seemed to become thinner, then thicker. It consisted of needles and did not dissolve on the addition of 250 cc. more of ice water. The suspension stood an hour and was then treated with 13 grams of potassium iodide in 25 cc. of water. After two hours the mixture was warmed. The yellowish material which separated was found to weigh 6.9 grams. This is 97 per cent. of the calculated. When this substance was boiled with water and the solution cooled, nothing but a mere turbidity was observed, the material remaining insoluble. It was purified by dissolving in hot alcohol, in which it is readily soluble, and then pouring into a large volume of water. The precipitate was then crystallized from 95 per cent. alcohol. It formed small, oblong tables or prisms which melted to a red oil at 235°–236°. The acid is precipitated from its solution in ammonia by acetic acid. It dissolves in benzene and crystallizes in wavy wisps of needles. From ether it separates in canoe-shaped, flat plates. When it was mixed with the 3,5-diiodbenzoic acid prepared from 3,5-diiod-4-aminobenzoic acid the melting point was not altered.

| | Calculated for $C_7H_4O_2I_2$. | Found. |
|---|---|---|
| I | 67.91 | 67.04 |

New Haven, Conn.,
May, 1909.

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[Contributions from the Sheffield Laboratory of Yale University.]

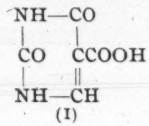
## CLXXV.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF 5-CYANURACIL.

[Forty-eighth paper.]

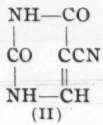
By Treat B. Johnson.

The present work was undertaken with the object of preparing some pyrimidines to be used for the syntheses of new

derivatives of thymine. I shall describe the preparation and properties of the nitrile of uracil-5-carboxylic acid (I), *viz.*, 5-cyanuracil (II), and some of its derivatives.



(I)



(II)

It has been shown in a previous paper from this laboratory[1] that diethyl ethoxymethylenemalonate,[2]

$$C_2H_5OCH : C(COOC_2H_5)_2,$$

condenses smoothly with pseudothioureas, $H_2NC(SR) : NH$, in aqueous solution, in the presence of alkali, giving 2-alkylmercapto-5-carboxyl-6-oxypyrimidines. Uracil-5-carboxylic acid (I) is then obtained easily by hydrolysis of these mercaptopyrimidines with acids. It seemed very probable to the writer that 5-cyanuracil (II) might be synthesized in an analogous manner from ethyl ethoxymethylenecyanacetate,

$$C_2H_5OCH : C(CN)COOC_2H_5.$$

DeBollemont[3] has described several esters of this character, which he has prepared by condensation of orthoformic esters, $CH(OR)_3$, with esters of cyanacetic acid in presence of acetic anhydride. He has also examined the behavior of several of them towards organic bases and shown that they react smoothly with formation of the corresponding amino derivatives,

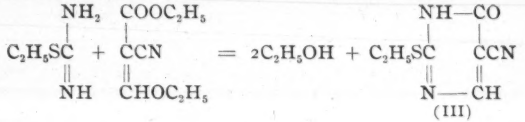
$$RHNCH : C(CN)COOR.$$

The action of ureas, thioureas, pseudoureas, and pseudothioureas on these esters, however, has not been investigated.

Ethyl ethoxymethylenecyanacetate was prepared for my experiments according to the directions of deBollemont.[4] I now find that pseudoethylthiourea condenses in alcoholic

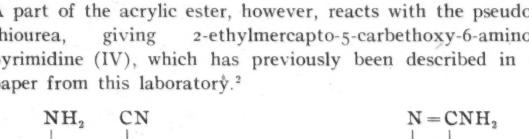
[1] THIS JOURNAL, **37**, 392 (1907).
[2] Claisen: Ann. Chem. (Liebig), **297**, 75 (1897).
[3] Compt. Rend., **128**, 1338; **129**, 5; Bull. Soc. Chim., [3] **25**, 18, 28, 39.
[4] *Loc. cit.*

solution with this ester, in the presence of alkali, in two ways, giving a mixture of two mercaptopyrimidines. The main reaction is a condensation with the ester, similar to that with diethyl ethoxymethylenemalonate,[1] giving 2-ethyl-mercapto-5-cyan-6-oxypyrimidine (III). This condensation is represented by the following equation:



(III)

A part of the acrylic ester, however, reacts with the pseudo-thiourea, giving 2-ethylmercapto-5-carbethoxy-6-amino-pyrimidine (IV), which has previously been described in a paper from this laboratory.[2]



(IV)

This interesting observation suggests that other cyanides containing the grouping $C_2H_5OCH : C(CN)$ will be found to condense with pseudothioureas, giving aminopyrimidines.

It is interesting to note here that ethyl acetylcyanacetate,

$$CH_3COCH(CN)COOC_2H_5,$$

does not condense with pseudoethylthiourea to give a pyrimidine.[3] On the other hand, it has been shown that the pseudoureas,[4] $H_2NC(OR) : NH$, condense with ethyl cyan-acetate, in presence of alkali, giving the corresponding 2-alkyl-oxy-4-amino-6-oxypyrimidines.[5]

[1] *Loc. cit.*

[2] Wheeler and Johns: THIS JOURNAL, **38**, 594.

[3] Wheeler: THIS JOURNAL, **28**, 358.

[4] Stieglitz and McKee: Ber. d. chem. Ges., **32**, 1494; **33**, 807, 1517; Stieglitz and Noble: *Ibid.*, **38**, 2243.

[5] Centrabl., **1904**, II, 631.

I also investigated the action of pseudoethylthiourea on ethyl ethoxymethylenecyanacetate (V) in alcohol containing no free alkali. When they were allowed to react under these conditions in molecular proportions, there was no evidence of the formation of 2-ethylmercapto-5-cyan-6-oxypyrimidine (III), and 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine (IV) and ethyl $\alpha$-cyan-$\beta$-pseudoethylthiourea-acrylate (VIII) were the only products of the reaction. If more than one molecular proportion of pseudoethylthiourea is used for the condensation the ethyl $\alpha$-cyan-$\beta$-pseudoethylthiourea-acrylate that is formed then reacts with the excess of pseudothiourea, giving $\alpha$-cyan-$\beta$-pseudoethylthiourea-acrylpseudoethylthiourea (VI).

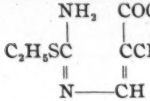
Ethyl $\alpha$-cyan-$\beta$-pseudoethylthiourea-acrylate (VIII) and $\alpha$-cyan-$\beta$-pseudoethylthiourea-acrylpseudoethylthiourea (VI) are both converted quantitatively into 2-ethylmercapto-5-cyan-6-oxypyrimidine (III) when warmed with alkali. A quantitative yield of 5-cyanuracil (XI) is then obtained by hydrolysis of this mercaptopyrimidine, in alcohol, with sulphuric acid. Attempts to hydrolyze this mercaptopyrimidine (III) smoothly to 5-cyanuracil, in aqueous solution, were unsuccessful. The nitrile group slowly undergoes hydrolysis under these conditions, giving a mixture of 5-cyanuracil (XI) and uracil-5-carboxamide (X). These are both converted quantitatively into uracil-5-carboxylic acid (IX) and finally into uracil (VII) by long digestion with concentrated hydrochloric acid. These various transformations are represented by the following formulas:

## EXPERIMENTAL PART.

*Ethyl Ethoxymethylenecyanacetate,* $C_2H_5OCH : C(CN)COOC_2H_5$.—This ester was prepared according to the directions given by de Bollemont.[1] It melts at 52°–53° and is insoluble in water but very soluble in alcohol, ether, and benzene.

*Condensation of Ethyl Ethoxymethylenecyanacetate with One Molecular Proportion of Pseudoethylthiourea in Alcohol.*

*Ethyl α-Cyan-β-pseudoethylthiourea-acrylate,*

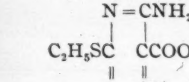


.—Molecular proportions of potassium hydroxide (0.45 gram) and the hydrobromide of pseudoethylthiourea (1.4 grams) were dissolved separately in 7 cc. of 95 per cent. alcohol, the solutions cooled to 0°, and combined. The undissolved potassium bromide was then separated quickly by filtration and 1.2 grams of ethyl ethoxymethylenecyanacetate added to the cold alcohol solution of pseudothiourea. The ester dissolved at once and within 1–2 minutes a yellow, crystalline substance separated. After standing a few minutes this was filtered off, washed thoroughly with ether, and the ether washings saved (see below). The substance obtained here, insoluble in ether, was the ethyl acrylate represented above and melted without further purification at 120°–125°. The ester is soluble in alcohol, insoluble in cold water and ether, and crystallizes from benzene in tufts of yellow distorted needles melting at 130° with slight effervescence. It separates from a hot aqueous solution as an oil, which finally crystallizes in colorless needles melting at the same temperature. Nitrogen (Kjeldahl):

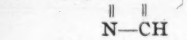
| | Calculated for $C_9H_{13}O_2N_3S$. | Found. |
|---|---|---|
| N | 18.50 | 18.7 |

[1] *Loc. cit.*

*2-Ethylmercapto-5-carbethoxy-6-aminopyrimidine*,



$C_2H_5SC\ \ CCOOC_2H_5$.—This pyrimidine was obtained when



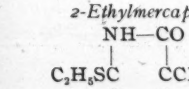
the ether solution described above was allowed to evaporate. It was insoluble in cold, dilute sodium hydroxide solution but soluble in hydrochloric acid, and crystallized from 95 per cent. alcohol in rectangular plates melting at 102°–103° to a clear oil with no effervescence. This same pyrimidine has previously been described by Wheeler and Johns.[1] A mixture of my derivative and their pyrimidine melted at 102°. Nitrogen (Kjeldahl):

| | Calculated for $C_9H_{13}O_2N_3S$. | Found. |
|---|---|---|
| N | 18.50 | 18.6 |

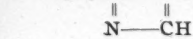
The comparative yields of the above acrylic ester and this 6-aminopyrimidine were irregular, but the ester was always the chief product of the reaction. They were apparently the only compounds formed under the conditions employed.

*Action of Alkali on Ethyl α-Cyan-β-pseudoethylthiourea-acrylate.*—This ester is not decomposed by cold, dilute sodium hydroxide solution. On the other hand, when warmed with alkali it immediately dissolved, giving the sodium salt of 2-ethylmercapto-5-cyan-6-oxypyrimidine. When the alkaline solution was acidified with hydrochloric acid,

*2-Ethylmercapto-5-cyan-6-oxypyrimidine*,



$C_2H_5SC\ \ CCN$, separated in colorless crystals melting at



218°–20° to an oil. It crystallizes from hot water in prisms, which melt at 222° to a clear oil without effervescence. The pyrimidine gives a strong test for uracil when treated with bromine water and barium hydroxide solution.[2] Nitrogen determinations (Kjeldahl):

[1] *Loc. cit.*

[2] Wheeler and Johnson: J. Biol. Chem., **3**, 183 (1907).

| | Calculated for $C_7H_7ON_3S$. | Found. I. | II. |
|---|---|---|---|
| N | 23.22 | 23.0 | 23.15 |

This pyrimidine and 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine are the only products of the reaction when pseudoethylthiourea is condensed with ethyl ethoxymethylenecyanacetate in alcohol in the presence of an excess of alkali.

*Condensation of Ethyl Ethoxymethylenecyanacetate with More than One Molecular Proportion of Pseudoethylthiourea in Alcohol.*

An alcoholic solution of pseudoethylthiourea was prepared by dissolving 20 grams of the hydrobromide of pseudoethylthiourea (1.7 mols.) in 70 cc. of absolute alcohol and then adding, at 0°, a solution of 6.1 grams of potassium hydroxide (1.7 mols.) in 30 cc. of 95 per cent. alcohol. After filtering from potassium bromide, 10.7 grams of ethyl ethoxymethylenecyanacetate (1 mol.) were added to the pseudourea solution at once when there was an immediate reaction and a thick mush of crystalline material was obtained. A portion of this material was filtered off and washed with ether. It then melted at 128°–130°. This insoluble substance was identified as ethyl α-cyan-β-pseudoethylthiourea-acrylate, which was obtained in my previous condensation (see above). On evaporating the ether solution I obtained 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine[1] which was identified by its melting point, 102°–103°.

The main portion of the reaction mixture, however, was allowed to stand, at ordinary temperature, for about 2–3 hours, when, to my surprise, practically all of the acrylic ester, with the exception of about 1–2 grams, had dissolved. The solution was then filtered, concentrated on the steam bath, and cooled when I obtained about 12–13 grams of crystalline material. This was washed with ether to remove any 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine, and then triturated with cold, dilute sodium hydroxide solution. I obtained 10.5 grams of a crystalline substance insoluble in the alkaline solution. It

[1] Wheeler and Johns: *Loc. cit.*

was soluble in hot water and alcohol and crystallized from hot water in well-developed prisms which melted at 164°–165° with effervescence. A nitrogen determination agreed with the calculated value for *α-cyan-β-pseudoethylthiourea-acrylpseudoethylthiourea*, $NH_2C(SC_2H_5):NCH:C(CN)CO.N:C(SC_2H_5)NH_2$.

| | Calculated for $C_{10}H_{15}ON_5S_2$. | Found. |
|---|---|---|
| N | 24.56 | 24.43 |

When the sodium hydroxide solution (above) was carefully acidified with hydrochloric acid, 2-ethylmercapto-5-cyan-6-oxypyrimidine separated. It crystallized in prisms melting at 222° to an oil. Analysis (Kjeldahl):

| | Calculated for $C_7H_7ON_3S$. | Found. |
|---|---|---|
| N | 23.22 | 23.0 |

*Action of Alkali on α-Cyan-β-pseudoethylthiourea-acrylpseudoethylthiourea.*

About 1.5 grams of this compound were warmed with 10 cc. of a 10 per cent. aqueous solution of sodium hydroxide for a few minutes. Ethyl mercaptan was evolved and the compound dissolved, giving a clear solution. When this was acidified with hydrochloric acid 2-ethylmercapto-5-cyan-6-oxypyrimidine separated in prisms melting at 220°–222°. Analysis (Kjeldahl):

| | Calculated for $C_7H_7ON_3S$. | Found. |
|---|---|---|
| N | 23.22 | 23.16 |

*Behavior with Hydrochloric Acid.*—One gram of α-cyan-β-pseudoethylthiourea-acrylpseudoethylthiourea was dissolved in about 40–50 cc. of concentrated hydrochloric acid and the solution evaporated to dryness. I obtained practically a quantitative yield of *5-cyanuracil* (see below) which melted without purification at 291°–293°. After one crystallization from water it melted at 293°–295° and a nitrogen determination (Kjeldahl) gave:

| | Calculated for $C_5H_3O_2N_3$. | Found. |
|---|---|---|
| N | 30.6 | 30.2 |

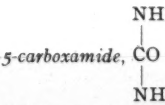
*2,6-Dioxy-5-cyanpyrimidine (5-Cyanuracil)*,

.—A quantitative yield of this pyrimidine was also obtained by hydrolysis of 2-ethylmercapto-5-cyan-6-oxypyrimidine with sulphuric acid as follows: 0.7 gram of the mercapto-pyrimidine was dissolved in a mixture of 30 cc. of alcohol and 3 cc. of concentrated sulphuric acid and the solution boiled until the evolution of ethyl mercaptan ceased. The 5-cyan-pyrimidine separated in hard, granular crystals melting at 291°–292°. It is difficultly soluble in cold alcohol and crystallizes from hot water in prisms which melt at 295° with decomposition. Analysis (Kjeldahl):

| | Calculated for $C_5H_3O_2N_3$. | Found. I. | Found. II. |
|---|---|---|---|
| N | 30.6 | 30.1 | 30.55 |

When this pyrimidine was digested with concentrated hydrochloric acid for several hours it was converted quantitatively into uracil. Analysis (Kjeldahl):

| | Calculated for $C_4H_4O_2N_2$. | Found. |
|---|---|---|
| N | 25.00 | 24.6 |



*Uracil-5-carboxamide*, .—One gram of 2-ethyl-mercapto-5-cyan-6-oxypyrimidine was dissolved in 50 cc. of concentrated hydrochloric acid and the solution evaporated to dryness on the steam bath. The crystalline material which was obtained was then dissolved in hot water and the solution cooled slowly, when this pyrimidine separated in small prisms. It is difficultly soluble in cold water and does not melt below 300°. It gives a strong test for uracil when treated with bromine water and barium hydroxide. After heating for 5 hours at 100°–110° a nitrogen determination (Kjeldahl) gave:

| | Calculated for $C_5H_5O_3N_3$. | Found. |
|---|---|---|
| N | 27.00 | 26.80 |

This amide was converted quantitatively into uracil when digested with concentrated hydrochloric acid.

The aqueous mother liquor (above), after being filtered from uracil-5-carboxamide, was concentrated to a small volume and cooled, when the characteristic prisms of 5-cyanuracil separated. After two crystallizations from hot water it melted at 293°–295°. Analysis (Kjeldahl):

| | Calculated for $C_5H_3O_2N_3$. | Found. |
|---|---|---|
| N | 30.6 | 30.1 |

NEW HAVEN, CONN.,
July, 1909.

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[Contribution from the Chemical Laboratory of the University of Cincinnati.]

## THE PREPARATION OF HYDROXAMIC ACIDS FROM HYDROXYLAMINE SALTS OF ORGANIC ACIDS.

BY LAUDER WILLIAM JONES AND RALPH OESPER.

A survey of the various methods which have been employed in the synthesis of hydroxamic acids will show that almost every one of them has its counterpart in some process used to obtain acid amides. The amides are frequently made by heating ammonium salts; it is singular, therefore, that this method, very generally successful in the making of amides, has not led to a similar procedure for the direct preparation of hydroxamic acids from hydroxylamine salts.[1]

In the course of some experiments with hydroxylamine formate, $HC(=O).ONH_3OH$, it was observed that a solution of this salt in acidulated water gave no color reaction with ferric chloride. When, however, the salt had been kept for several weeks, or had been heated for a few minutes to its melting point (76°), and was subsequently dissolved in water, the addition of an acidulated solution of ferric chloride caused an intense purple color identical with that produced when a solution of formhydroxamic acid was treated with ferric chloride under similar conditions. It was evident that heat

[1] Ssabanejeff: J. russ. physik. chem. Ges., **31**, 377; Centralb., **1899**, II, 33. This author mentions incidentally that the hydroxylamine salt of succinamic acid, $H_2N.CO.C_2H_4.CO.ONH_3.OH$, passed into the corresponding hydroxamic acid when it had been kept for a long time or had been heated to its boiling point.

had accelerated the change of the hydroxylamine salt into formhydroxamic acid, a transformation which proceeded with measurable velocity at ordinary room temperature.

$$HC(=O).ONH_3.OH \rightleftarrows HC(=O).NH(OH) + H_2O.$$

But unfortunately, the ease with which formhydroxamic acid dissociates into free hydroxylamine and carbon monoxide made it impracticable to carry out this reaction at temperatures even a few degrees above the melting point of the formate without causing considerable or total destruction of the hydroxamic acid expected:[1]

$$HN(OH).C(=O)H \rightleftarrows H_2NOH + C=O.$$

That this reaction would prove to be reversible seemed quite plausible in view of the abundant analogy furnished by the many reversible reactions known to occur when carbon monoxide and various reagents interact.[2] To establish the correctness of this conclusion, a stream of carbon monoxide was passed through free hydroxylamine for several hours. A product resulted which, with ferric chloride, gave the usual test for hydroxamic acid.

To try the new method of making hydroxamic acids under more favorable conditions, the use of hydroxylamine acetate seemed more promising than the formate; but in this case also, the hydroxamic acid was found to undergo decomposition even below 100°. Nevertheless, at a temperature of 90°, a fairly successful synthesis of acethydroxamic acid was effected.

$$CH_3C(=O)ONH_3OH \rightleftarrows CH_3C(=O)NHOH + H_2O.$$

This reaction is undoubtedly reversible, and would reach a condition of equilibrium similar to that observed by Menschutkin[3] in the case of ammonium acetate and acetamide, were it not for the complication that both acethydroxamic acid and hydroxylamine acetate dissociate slowly in other ways, with the result that at 90°, with a two-gram sample,

[1] Jones: THIS JOURNAL, **20**, 29; Biddle: Ann. Chem. (Liebig), **310**, 14.

[2] DeLambelly: D. R. P. 78573 ($NH_2$ + CO); Loeb: Z. Elek. Chem., **11**, 745 (CO + $H_2O$); **12**, 282 (CO + $H_2$).

[3] Menschutkin: J. prakt. Chem., [2] **29**, 422.

the amount of hydroxamic acid apparently reached a maximum when about 30 per cent. of the calculated quantity was present. From this point on, the contending decompositions proceeded in such a manner that the amount of hydroxamic acid finally obtained was rapidly diminished as the time of heating increased.

No simple method of separating the products by fractional crystallization from solvents could be found. By means of a solution of copper acetate, a precipitate was produced which consisted of cuprous oxide (due to reduction by the hydroxylamine salt) and the basic copper salt of acethydroxamic acid, $C_4H_8O_5N_2Cu_2$, described by Crismer.[1] From this mixture, pure acethydroxamic acid was prepared in the usual way by passing hydrogen sulphide through alcohol in which the copper salt was suspended.

Rough experiments have shown that hydroxylamine benzoate and hydroxylamine anisate, at temperatures slightly above their melting points, also yield the corresponding hydroxamic acids.

## EXPERIMENTAL.

*Hydroxylamine Formate.*—Ssabanejeff[2] prepared this compound by the action of hydroxylamine sulphate upon barium formate. It was made more readily in a pure condition by the action of the calculated amount of anhydrous formic acid upon a weighed quantity of hydroxylamine surrounded by a freezing mixture. Considerable heat was evolved, and the product soon solidified. After an hour, the salt was drained by filtration, dried and recrystallized from alcohol. The nitrogen content was determined.

0.2595 gram gave 42.6 cc. of nitrogen at 23° and 732.4 mm.

| | Calculated for $CH_3O_2N$. | Found. |
|---|---|---|
| N | 17.72 | 17.75 |

*Properties of Hydroxylamine Formate.*—The salt crystallized in colorless needles which melted at 76°. It was soluble in water and in hot alcohol, but almost insoluble in ether or

[1] Crismer: Bull. Soc. Chim., [3] **3**, 121.
[2] *Loc. cit.*

ligroin. When heated to a temperature between 78° and 80° for a short time, the fused residue gave a decided test for hydroxamic acid. If the heating was continued longer, or if the temperature rose above 80°, violent decomposition set in at once. In open vessels, the salt was observed to lose weight quite rapidly, possibly because of sublimation or dissociation, or through both causes at the same time. A sample of the salt which had stood in a desiccator over calcium chloride for several weeks was found to contain a large amount of formhydroxamic acid.

*Synthesis of Formhydroxamic Acid from Carbon Monoxide and Hydroxylamine.*—About 5 grams of free hydroxylamine were placed in a Liebig's absorption apparatus, and a stream of pure, dry carbon monoxide was passed through it slowly for seven hours. When acidified with dilute sulphuric acid, the reaction product gave a decided purple color with ferric chloride; but this color faded away almost instantly. It has been shown that ferric salts are easily reduced by hydroxylamine salts in acid solution. The reaction in the case of ferric chloride is expressed by the following equation:

$$4FeCl_3 + 2NH_2OH = 4FeCl_2 + N_2O + H_2O + 4HCl.$$

Ferric salts of hydroxamic acids would not be exceptions to this rule. A solution of pure formhydroxamic acid was treated with an acid solution of ferric chloride; when some hydroxylamine was added, the purple color was instantly discharged.

The amount of formhydroxamic acid produced by the method described must have been very small. Experiments will be tried in which hydroxylamine will be allowed to act upon carbon monoxide under considerably increased pressures.

*Hydroxylamine Acetate.*—The salt employed in the following experiments was made by dropping the calculated weight of glacial acetic acid into free hydroxylamine cooled by ice. After the salt had been recrystallized from hot alcohol, it was found to be identical with the compound described by Lossen.[1]

[1] Lossen: Ann. Chem. (Liebig), Supp., **6**, 231.

Experiments performed in open vessels soon showed that the salt, at temperatures between 88° and 90°, sublimed so rapidly that the heat could not be applied in a satisfactory manner. To obviate this difficulty, weighed samples were placed in test tubes which, after being sealed, were heated to a temperature of 90° for different periods of time varying from one to eight hours.

When the tubes were opened, a small quantity of colorless gas escaped, and the odor of acetic acid was very noticeable. The contents of each tube were dissolved in water, and each solution was treated separately with a slight excess of a saturated solution of cupric acetate, which immediately produced a precipitate composed of cuprous oxide and the basic copper salt of acethydroxamic acid.

These precipitates were dried at a temperature of 110°, and weighed. The percentage of nitrogen in each was then determined by analysis. Upon the assumption that all of the nitrogen present in the precipitates was combined as the basic copper salt of acethydroxamic acid, $C_4H_8O_5N_2Cu_2$, the amount of acethydroxamic acid which each precipitate represented could be estimated. The results of the analyses were as follows:

| Sample. | *a.* | *b.* | *c.* |
|---|---|---|---|
| Wt. of sample (gram) | 0.5000 | 0.5000 | 0.3925 |
| Volume of nitrogen (cc.) | 24.2 | 36.1 | 28.3 |
| Temperature (°) | 24.5 | 23.5 | 23.0 |
| Pressure (mm.) | 741.6 | 741.5 | 739.6 |
| Percentage of nitrogen | 5.31 | 7.93 | 7.94 |

| | *d.* | *e.* | *f.* |
|---|---|---|---|
| Wt. of sample (gram) | 0.3469 | 0.3786 | 0.3342 |
| Volume of nitrogen (cc.) | 30.5 | 33.0 | 29.8 |
| Temperature (°) | 24.0 | 24.0 | 18.0 |
| Pressure (mm.) | 744.4 | 737.5 | 728.9 |
| Percentage of nitrogen | 9.7 | 9.49 | 9.83 |

The percentage yields of acethydroxamic acid calculated from these results are given in the following table:

| Sample. | *a.* | *b.* | *c.* |
|---|---|---|---|
| Weight in grams | 2 | 2 | 2 |
| Period of heating (hours) | 1 | 2 | 3 |
| Weight of copper salts | 1.59 | 1.07 | 1.10 |
| Percentage of nitrogen | 5.31 | 7.93 | 7.94 |
| Weight of acid | 0.451 | 0.453 | 0.467 |
| Percentage yield of acid | 28.0 | 28.1 | 29.0 |

| Sample. | *d.* | *e.* | *f.* |
|---|---|---|---|
| Weight in grams | 2 | 2 | 2 |
| Period of heating (hours) | 3.5 | 3.75 | 4.5 |
| Weight of copper salts | 0.91 | 0.85 | 0.77 |
| Percentage of nitrogen | 9.70 | 9.49 | 9.33 |
| Weight of acid | 0.493 | 0.428 | 0.401 |
| Percentage yield of acid | 30.6 | 26.5 | 24.9 |

These figures show that the conditions represented in column *d* were the most favorable for obtaining a large amount of acethydroxamic acid, when 2-gram samples were heated at 90°.

Several dried samples of the mixture of cuprous oxide and basic copper salt were suspended in methyl alcohol, and treated with hydrogen sulphide. When the alcoholic solution, separated from copper sulphide, was evaporated *in vacuo*, solid acethydroxamic acid remained. It was identical in properties with the compound prepared by Lossen.

## THE EFFECT OF TEMPERATURE AND DILUTION ON THE CONDUCTIVITY OF ORGANIC ACIDS IN AQUEOUS SOLUTION.

By George F. White and Harry C. Jones.

A thoroughly systematic study of the conductivity and dissociation of organic acids, as affected by temperature as well as by dilution, has not been made since this important method of determining the strength of electrolytes has come into use. There are a few articles in the literature which deal with this subject, but a comprehensive investigation of the field is lacking, and many of the conclusions that have been reached are conflicting. In the brief review presented

here of work dealing with conductivity and dissociation at various temperatures, attention will be called mainly to matter dealing with the subject in hand, that is, the organic acids. Comparatively little reference will be made to the enormous amount of work carried out at one temperature.

It was early observed that the conductivity of electrolytes in solution changes with the temperature, and in the reverse sense to that of metals. This fact was long known without accurate or extended measurements being made to further our knowledge of the subject. Over sixty years ago Ohm[1] and Becquerel[2] pointed out a few facts concerning the effect of temperature on conductivity. Hankel,[3] in a piece of work of wider scope than any preceding it, showed that the electrical resistance of many solutions very noticeably decreased with rising temperature, and he worked out a few general relations connecting the behavior of various substances.

E. Becker[4] in 1850 studied the conductivity of solutions of a few of the common acids and salts between 0° and 100°, formulating some of his results in equations connecting temperature and conductivity. Later[5] he investigated the effect of concentration. Attention may also be called to the work of Beetz,[6] Freund,[7] Bergren,[8] Long[9] and Bouty.[10]

The first serious and important investigation was completed in 1874 by Grotrian,[11] who studied the conductivity of solutions of hydrochloric acid and sulphuric acid, use being made of the alternating current method of Kohlrausch. Grotrian found that the conductivity of the hydrochloric acid solution was a linear function of the temperature between 0° and 33°, but he obtained a parabolic interpolation formula for sulphuric acid between 0° and 70°. A maximum in conductivity

[1] Pogg. Ann., **63**, 403 (1844).
[2] *Ibid.*, **70**, 254 (1847).
[3] *Ibid.*, **69**, 255 (1846).
[4] Ann. Chem. (Liebig). **73**, 1 (1850).
[5] *Ibid.*, **75**, 94 (1850).
[6] Pogg. Ann., **117**, 1 (1862).
[7] Wied. Ann., **7**, 49 (1879).
[8] *Ibid.*, **1**, 499 (1877).
[9] *Ibid.*, **11**, 37 (1880).
[10] Ann. Chim. Phys., [6] **3**, 498 (1884).
[11] Pogg. Ann., **151**, 378 (1874).

occurred at a definite dilution, which in the case of sulphuric acid became greater the higher the temperature. The solution of hydrochloric acid behaved in the opposite sense. This work was followed by that of Kohlrausch and Grotrian[1] in which were investigated many electrolytes, including nitric acid and some alkali and alkaline earth salts. They concluded that it is a practically general truth that in dilute solutions conductivity is a parabolic function of the temperature. They applied the ordinary equation of the parabola,

$$K_t = K_o(1 + \alpha t + \beta t^2),$$

in which $\alpha$ and $\beta$ are constants depending on the nature of the electrolyte, and easily calculated, and $K_t$ and $K_o$ are the conductivities at $t°$ and $o°$, respectively.

In 1887 Otten[2] studied the influence of temperature on the conductivity of some fatty acids. He used formic, acetic, propionic and butyric acids, and showed that the resistance increases as we go up in the homologous series. In the case of all the acids, the conductivity increased with the percentage content of the solution up to a maximum and then decreased. The maximum for formic acid lay at a concentration of about 30 per cent., and for the higher members in the series it occurred at a lower concentration.

Arrhenius[3] measured the conductivity of various electrolytes in dilute solutions at 18° and 52°, and by means of the formula

$$\mu_{52} = \mu_{18}\,(1 + \alpha_{35}^{0.34}),$$

in which $\mu$ is the molecular conductivity and $\alpha$ the temperature coefficient, he was able to calculate the mean temperature coefficient between these temperatures. The temperature coefficients of the more strongly dissociated electrolytes are generally smaller the greater the conductivity; hence the conductivities approach one another as the temperature rises. The change of the coefficients with the strength of the solution is not great so long as the latter remains small. Arrhenius also observed an exceedingly important fact, *viz.*, that the

[1] Pogg. Ann., **154**, 215 (1875).
[2] Diss., München (1887).
[3] Z. physik. Chem., **4**, 96 (1889).

dissociation of phosphoric and hypophosphorous acids decreases with rise in temperature. This was a surprising discovery in the light of the old theory, which explained increase in conductivity with rise in temperature on the assumption of increase in dissociation. This question of the influence of temperature on dissociation has remained a subject of study up to the present day, and still needs a large amount of further investigation.

The work of Krannhals[1] may be mentioned here. He discovered few new relations in his study of the conductivity of some typical acids and salts, and his results generally confirmed the conclusions of Kohlrausch and Grotrian. He concluded that temperature has no effect on dissociation.

In 1895 Hans Jahn and E. Schröder[2] made determinations of the conductivity of aqueous solutions of formic, acetic, propionic, butyric, isobutyric and valeric acids. Each acid was investigated in solutions varying from N/2 to N/128, and at a series of temperatures ranging from 10° to 50°. They expressed their results by interpolation formulae, calculated values agreeing satisfactorily with those observed. Their method of work was not sufficiently accurate to enable them to notice a change in dissociation with temperature, and they infer therefore that it is constant. Their results, however, show a decreasing dissociation with rise in temperature in the case of valeric acid, but they assumed this to be due to the presence of impurities. Jahn therefore concluded that increase in conductivity with the temperature is a function of the decrease of ionic friction. Déguisne[3] and Wood[4] also worked in the field at this time.

In 1896 Euler[5] studied some typical aromatic organic acids between 10° and 50° and at various dilutions. Interpolation formulae were calculated for each acid at every dilution and were found to be of the form

$$\lambda = a + bt - ct^2,$$

[1] Z. physik. Chem., **5**, 250 (1890).
[2] *Ibid.*, **16**, 72 (1895).
[3] Diss., Strassbourg (1895).
[4] Phil. Mag., **41**, 117 (1896).
[5] Z. physik. Chem., **21**, 257 (1896).

where $\lambda$ represents the molecular conductivity and $t$ the temperature. The form of the equation indicates a maximum in the curve if the expression applies at higher temperatures. In every case the dissociation varied with the temperature, a maximum occurring for benzoic acid at about 25°, and for *m*-hydroxybenzoic acid at about 28°. The values for toluic acid decreased with rising temperature, but those for *m*-nitrobenzoic and salicylic acids increased. Euler offered no explanation for these inharmonious results, and further investigation seems necessary on this subject before the work can be accepted as final. There is no apparent reason why *m*-hydroxybenzoic and benzoic acid should differ so fundamentally in their behavior, and the other relations seem inconsistent.

Schaller[1] studied the conductivity of several acids, bases and salts, including a few organic acids. He made use of platinum vessels to avoid the solvent action of water on glass at the high temperatures at which he worked. The molecular conductivities were found to increase with rise in temperature, but at a diminishing rate, so that in some cases a maximum was reached, beyond which the molecular conductivity decreased. The degree of dissociation, however, in all cases decreased with rise in temperature.

In 1901 Jones and Douglas[2] measured the conductivity of a number of inorganic acids, bases and salts between 0° and 35°. They observed that for salts the temperature coefficients increase with rise in temperature, but noticed little change for acids and bases. Their results showed that temperature affects dissociation to no appreciable extent.

The work of Jones and West[3] and of Jones and Jacobson[4] at temperatures ranging from 0° to 35°, and of Noyes[5] at high temperatures, has established conclusively that dissociation decreases with rise in temperature for most of the substances they investigated. Jacobson obtained this result with a few organic

[1] Z. physik. Chem., **25**, 497 (1898).
[2] This Journal, **26**, 428 (1901).
[3] *Ibid.*, **34**, 357 (1905).
[4] *Ibid.*, **40**, 355 (1908).
[5] J. Am. Chem. Soc., **26**, 134 (1904).

acids, but found an increasing dissociation with rising temperature in the case of *m*-nitrobenzoic acid and a few inorganic salts. He suggests that this was due to the influence of hydrolysis. Molecular conductivity has been shown to be in general (water being a marked exception) a parabolic function of the temperature,[1] a state of things which may be explained by the theory of hydration which Jones has put forward as a result of considerable work by himself and students. According to this theory, it would appear that all electrolytes in aqueous solution are hydrated to a certain extent, a condition which would prevent conductivity from being a linear function of the temperature, as it very probably would be if the viscosity of the medium alone were the influencing factor. He sums up the facts now known in a recent paper[2] to which attention is here called.

From what has been said of the work already done, it is evident that more accurate and more extended data on the conductivity of organic acids as affected by temperature, at least between 0° and 35°, should be obtained. It is intended in this preliminary paper to supply this deficiency for a number of typical acids of both the aliphatic and aromatic series, and it is hoped by further investigation to supplement these and make the work as complete as practicable. The dissociation of these acids from 0° to 35° is reserved also for a future article. To obtain the conductivity at infinite dilution necessary for this purpose, the Kohlrausch method, which involves the use of the sodium salts of these organic acids, is being employed.

## EXPERIMENTAL PART.

The measurements were carried out by means of the ordinary Kohlrausch method with a Wheatstone bridge, rheostat, induction coil and telephone receiver. The bridge wire and thermometers were calibrated carefully, the latter to within 0°.01. All flasks, burettes and pipettes were calibrated for 20°. The conductivity cells were of the type used by

[1] THIS JOURNAL, **40**, 402 (1908).
[2] *Ibid.*, **41**, 19 (1909).

Jones and Bingham[1] and which have given satisfactory results in this laboratory for several years.

The measurements were made at four temperatures ranging from 0° to 35°, and at various dilutions from N/2 up to N/2048, or as near this strength as possible, this being dependent on the solubility of the acid.

The 0° bath was that made use of by Jacobson,[2] and fully described in his article, bearing on this same subject. The cells containing the solutions which it was desired to bring to a temperature between 0° and 25° were placed in a tank through which tap water was kept flowing and stirred by its own pressure. Satisfactory results were obtained by this method, no measurements being taken until the temperature was observed to be constant within 0.°03 for at least half an hour.

The 25° and 35° baths were heated by Bunsen burners. No automatic regulator was used, the size of the flame being easily regulated by a pinchcock, so that the maximum variation in temperature was no greater than 0.°02. The baths were stirred by paddles rotated by hot-air engines.

It was necessary for the cells to remain for at least an hour in those baths kept at and below a temperature of 25°. At 35°, however, the solutions gave constant readings in the short space of half an hour. Duplicate readings were taken after an interval of five minutes to insure constant temperature. The final results also were the average of three measurements, taken with the minimum as near the center of the bridge as convenient. As few plugs as possible were removed from the resistance box.

*Organic Acids.*—The organic acids in most instances were obtained from Kahlbaum. They were purified by crystallization or distillation, as was most suitable, and tested as to their purity by their melting points or boiling points. The liquids were made up into solutions which were standardized by potassium hydroxide dissolved in absolute alcohol, phenolphthalein being employed as the indicator. As the acid was

[1] THIS JOURNAL, **34**, 481 (1905).
[2] *Ibid.*, **40**, 355 (1908).

dissolved in conductivity water, the absence of carbonic acid was thus assured, and the titration made reliable. The most concentrated solution being brought to the desired normality, the more dilute solutions were made up from this. The solutions of the solid acids were obtained in the same manner, the mother solution being made up by weight and standardized by titration.

*Cell Constants.*—The cell constants were obtained in the usual manner by the aid of a N/50 solution of pure potassium chloride. Kohlrausch's value for the molecular conductivity of this solution is 129.7 (Siemen's units); adding to this the amount due to the conductivity of the water, the constants can easily be calculated. For those cells in which the platinum plates were close together a N/500 solution of potassium chloride was used, the conductivity of which was measured in the cells standardized with the N/50 solution. The constants were redetermined frequently although absolutely no change, within the limits of experimental error, was found in many for several months. With due caution as to removing the electrodes from the cell cups this result is assured, and more reliance can be placed on the measurements. At the temperatures at which we worked there was no noticeable effect due to the solubility of the glass.

*Water.*—The conductivity water employed in making up the solutions was distilled according to the method previously used in this laboratory and frequently described. The process consists simply in the distillation of ordinary distilled water from a potassium bichromate solution acidified with sulphuric acid, to destroy organic matter and retain ammonia. The distillate is then distilled from a flask containing barium hydroxide, and finally redistilled through a block tin condenser, the last two operations being carried out in one piece of apparatus. The water thus obtained had a conductivity at 25° varying from $1.2 \times 10^{-6}$ to $1.7 \times 10^{-6}$. It was kept in glass bottles long used for the purpose, and withdrawn by a siphon and protected from carbon dioxide in the air by soda-lime.

*Results.*—The results are tabulated in the following pages,

molecular conductivities ($\mu_v$) being expressed in Siemen's units. The dissociation ($\alpha$) at 25° was calculated by the aid of Ostwald's values for the conductivity at infinite dilution. The temperature coefficients expressed in conductivity units and in percentages need no explanation.

*Table I.—Acetic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 9.°2. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 2 | 1.270 | 1.560 | 2.089 | 0.57 | 2.359 |
| 8 | 2.656 | 3.292 | 4.342 | 1.19 | 4.948 |
| 32 | 5.328 | 6.612 | 8.699 | 2.39 | 9.912 |
| 128 | 10.48 | 13.04 | 17.11 | 4.69 | 19.46 |
| 512 | 20.45 | 25.40 | 33.24 | 9.11 | 37.75 |
| 1024 | 28.03 | 34.95 | 45.87 | 12.57 | 52.09 |
| 2048 | 39.05 | 48.65 | 63.00 | 17.26 | 70.89 |

*Temperature Coefficients.*

| | 0°—9.°2. | | 9.°2—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 2 | 0.03 | 2.49 | 0.03 | 2.15 | 0.03 | 1.30 |
| 8 | 0.07 | 2.61 | 0.07 | 2.02 | 0.06 | 1.40 |
| 32 | 0.14 | 2.62 | 0.13 | 2.00 | 0.12 | 1.39 |
| 128 | 0.28 | 2.66 | 0.26 | 1.98 | 0.24 | 1.37 |
| 512 | 0.54 | 2.63 | 0.50 | 1.96 | 0.45 | 1.36 |
| 1024 | 0.72 | 2.57 | 0.69 | 1.95 | 0.62 | 1.32 |
| 2048 | 1.04 | 2.67 | 0.91 | 1.87 | 0.79 | 1.25 |

*Table II.—Propionic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 6.°9. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 2 | 1.030 | 1.217 | 1.700 | 0.47 | 1.913 |
| 8 | 2.291 | 2.700 | 3.704 | 1.03 | 4.207 |
| 32 | 4.631 | 5.450 | 7.436 | 2.07 | 8.422 |
| 128 | 9.004 | 10.60 | 14.57 | 4.06 | 16.50 |
| 512 | 17.47 | 20.59 | 28.40 | 7.91 | 32.14 |
| 1024 | 23.82 | 28.03 | 38.94 | 10.85 | 44.06 |
| 2048 | 33.43 | 39.24 | 53.47 | 14.89 | 60.28 |

*Temperature Coefficients.*

| | 0°—6.°9. | | 6.°9—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 2 | 0.03 | 2.63 | 0.03 | 2.19 | 0.02 | 1.25 |
| 8 | 0.06 | 2.59 | 0.06 | 2.05 | 0.05 | 1.36 |
| 32 | 0.12 | 2.56 | 0.11 | 2.01 | 0.10 | 1.33 |
| 128 | 0.23 | 2.58 | 0.22 | 2.07 | 0.19 | 1.32 |
| 512 | 0.45 | 2.59 | 0.43 | 2.10 | 0.37 | 1.32 |
| 1024 | 0.61 | 2.56 | 0.59 | 2.11 | 0.51 | 1.31 |
| 2048 | 0.84 | 2.52 | 0.79 | 2.01 | 0.68 | 1.27 |

*Table III.*—n-*Butyric Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 9.°4. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu$ | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 2 | 1.090 | 1.341 | 1.730 | 0.49 | 1.930 |
| 8 | 2.501 | 3.062 | 3.891 | 1.09 | 4.351 |
| 32 | 5.072 | 6.230 | 7.902 | 2.22 | 8.801 |
| 128 | 10.00 | 12.23 | 15.45 | 4.34 | 17.14 |
| 512 | 19.44 | 23.79 | 29.86 | 8.39 | 33.00 |
| 1024 | 26.82 | 32.83 | 41.22 | 11.60 | 45.26 |
| 2048 | 37.37 | 45.63 | 57.20 | 15.96 | 62.71 |

*Temperature Coefficients.*

| | 0°—9.°4. | | 9.°4—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 2 | 0.03 | 2.44 | 0.03 | 1.87 | 0.02 | 1.16 |
| 8 | 0.06 | 2.38 | 0.05 | 1.74 | 0.05 | 1.19 |
| 32 | 0.12 | 2.43 | 0.11 | 1.72 | 0.09 | 1.14 |
| 128 | 0.24 | 2.44 | 0.21 | 1.69 | 0.17 | 1.09 |
| 512 | 0.46 | 2.38 | 0.39 | 1.64 | 0.31 | 1.05 |
| 1024 | 0.64 | 2.38 | 0.54 | 1.64 | 0.40 | 0.98 |
| 2048 | 0.88 | 2.35 | 0.74 | 1.61 | 0.55 | 0.96 |

*Table IV.*—*Phenylacetic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 13.°25. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 32 | 9.001 | 11.762 | 14.151 | 4.00 | 15.90 |
| 128 | 17.82 | 23.39 | 27.96 | 7.88 | 31.26 |
| 512 | 33.35 | 43.51 | 52.39 | 14.76 | 58.55 |
| 1024 | 45.68 | 59.59 | 71.63 | 20.18 | 79.84 |
| 2048 | 61.00 | 79.49 | 95.50 | 26.87 | 106.3 |

*Temperature Coefficients.*

| | 0°—13.°25. | | 13.°25—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent |
| 32 | 0.21 | 2.32 | 0.20 | 1.73 | 0.18 | 1.23 |
| 128 | 0.41 | 2.32 | 0.40 | 1.70 | 0.33 | 1.18 |
| 512 | 0.77 | 2.30 | 0.76 | 1.72 | 0.62 | 1.18 |
| 1024 | 1.05 | 2.30 | 1.03 | 1.72 | 0.82 | 1.15 |
| 2048 | 1.40 | 2.29 | 1.36 | 1.71 | 1.08 | 1.13 |

*Table V.—Malonic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 4.°9. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 2 | 11.81 | 13.34 | 19.61 | 5.48 | 22.51 |
| 8 | 23.19 | 26.20 | 38.40 | 10.67 | 44.03 |
| 32 | 43.51 | 49.25 | 72.23 | 20.18 | 82.55 |
| 128 | 78.30 | 88.83 | 129.8 | 36.26 | 148.2 |
| 512 | 127.1 | 143.4 | 208.7 | 58.30 | 237.4 |
| 1024 | 153.3 | 173.2 | 251.2 | 70.17 | 284.8 |
| 2048 | 176.9 | 199.1 | 289.1 | 80.76 | 326.6 |

*Temperature Coefficients.*

| | 0°—4.°9. | | 4.°9—25°. | | 25°—35° | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 2 | 0.31 | 2.64 | 0.31 | 2.34 | 0.29 | 1.48 |
| 8 | 0.61 | 2.66 | 0.61 | 2.32 | 0.58 | 1.47 |
| 32 | 1.17 | 2.69 | 1.14 | 2.32 | 1.03 | 1.43 |
| 128 | 2.09 | 2.67 | 2.04 | 2.30 | 1.84 | 1.42 |
| 512 | 3.33 | 2.62 | 3.25 | 2.27 | 2.87 | 1.38 |
| 1024 | 4.06 | 2.65 | 3.88 | 2.24 | 3.36 | 1.34 |
| 2048 | 4.53 | 2.56 | 4.48 | 2.25 | 3.75 | 1.30 |

*Table VI.—Succinic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 5.°7. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 8 | 4.570 | 5.371 | 8.032 | 2.25 | 9.251 |
| 32 | 9.211 | 10.72 | 16.01 | 4.50 | 18.36 |
| 128 | 18.24 | 21.35 | 31.24 | 8.78 | 35.80 |
| 512 | 34.75 | 40.59 | 59.34 | 16.62 | 67.87 |
| 1024 | 47.89 | 55.91 | 81.31 | 22.84 | 92.89 |
| 2048 | 64.61 | 75.29 | 109.6 | 30.80 | 124.8 |

*Temperature Coefficients.*

| | 0°–5.°7. | | 5.°7–25°. | | 25°–35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 8 | 0.14 | 3.07 | 0.14 | 2.57 | 0.12 | 1.52 |
| 32 | 0.28 | 3.03 | 0.27 | 2.56 | 0.24 | 1.47 |
| 128 | 0.55 | 2.99 | 0.51 | 2.40 | 0.46 | 1.46 |
| 512 | 1.02 | 2.95 | 0.97 | 2.39 | 0.85 | 1.44 |
| 1024 | 1.41 | 2.94 | 1.32 | 2.36 | 1.16 | 1.42 |
| 2048 | 1.87 | 2.90 | 1.78 | 2.36 | 1.52 | 1.39 |

*Table VII.—o-Phthalic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 8.°23. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 64 | 55.98 | 66.45 | 85.92 | 24.28 | 96.48 |
| 128 | 74.56 | 88.32 | 114.8 | 32.43 | 128.9 |
| 512 | 122.3 | 145.7 | 189.2 | 53.46 | 212.5 |
| 1024 | 148.2 | 177.1 | 231.9 | 65.48 | 259.7 |
| 2048 | 174.2 | 208.4 | 272.7 | 77.03 | 306.0 |

*Temperature Coefficients.*

| | 0°–8.°23. | | 8.°23–25°. | | 25°–35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 64 | 1.27 | 2.27 | 1.16 | 1.75 | 1.06 | 1.23 |
| 128 | 1.67 | 2.24 | 1.58 | 1.79 | 1.41 | 1.23 |
| 512 | 2.84 | 2.33 | 2.59 | 1.78 | 2.33 | 1.23 |
| 1024 | 3.51 | 2.37 | 3.27 | 1.85 | 2.78 | 1.20 |
| 2048 | 4.16 | 2.39 | 3.83 | 1.84 | 3.33 | 1.22 |

*Table VIII.—Benzoic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 15.°8. | 35° | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 64 | 13.42 | 19.08 | 22.29 | 6.26 | 25.40 |
| 128 | 18.79 | 26.93 | 31.39 | 8.82 | 35.71 |
| 512 | 36.00 | 51.30 | 59.79 | 16.79 | 67.81 |
| 1024 | 47.63 | 68.33 | 79.56 | 22.36 | 90.11 |
| 2048 | 64.95 | 91.30 | 106.0 | 29.78 | 119.7 |

*Temperature Coefficients.*

| | 0°—15.°8. | | 15.°8—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 64 | 0.36 | 2.67 | 0.35 | 1.83 | 0.31 | 1.40 |
| 128 | 0.50 | 2.66 | 0.49 | 1.81 | 0.43 | 1.38 |
| 512 | 0.97 | 2.69 | 0.92 | 1.81 | 0.80 | 1.35 |
| 1024 | 1.26 | 2.64 | 1.22 | 1.79 | 1.06 | 1.33 |
| 2048 | 1.67 | 2.57 | 1.60 | 1.75 | 1.37 | 1.30 |

*Table IX.—Salicylic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 6.°9. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 64 | .... | .... | 80.50 | 22.55 | 92.80 |
| 128 | 62.65 | 75.59 | 108.3 | 30.33 | 125.1 |
| 512 | 105.4 | 126.4 | 181.2 | 50.76 | 207.0 |
| 1024 | 130.7 | 156.9 | 223.2 | 62.52 | 255.4 |
| 2048 | 153.8 | 183.9 | 259.9 | 72.80 | 295.7 |

*Temperature Coefficients.*

| | 0°—6.°9. | | 6.°9—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 64 | .. | .. | .. | .. | 1.23 | 1.53 |
| 128 | 1.88 | 2.99 | 1.83 | 2.42 | 1.68 | 1.55 |
| 512 | 3.12 | 2.96 | 3.00 | 2.37 | 2.58 | 1.42 |
| 1024 | 3.80 | 2.91 | 3.63 | 2.31 | 3.22 | 1.41 |
| 2048 | 4.36 | 2.84 | 4.16 | 2.26 | 3.58 | 1.38 |

*Table X.—Gallic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 6.°5. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 64 | 9.790 | 11.66 | 16.90 | 4.75 | 19.36 |
| 128 | 14.01 | 16.55 | 23.60 | 6.63 | 27.10 |
| 512 | 28.89 | 34.08 | 48.33 | 13.58 | 55.12 |
| 1024 | 37.84 | 44.63 | 62.50 | 17.56 | 71.18 |
| 2048 | 51.50 | 60.72 | 85.02 | 23.89 | 96.7 |

*Temperature Coefficients.*

| | 0°—6.°5. | | 6.°5—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 64 | 0.29 | 2.94 | 0.28 | 2.43 | 0.25 | 1.46 |
| 128 | 0.39 | 2.79 | 0.38 | 2.30 | 0.35 | 1.48 |
| 512 | 0.80 | 2.77 | 0.77 | 2.26 | 0.68 | 1.41 |
| 1024 | 1.05 | 2.76 | 0.97 | 2.17 | 0.87 | 1.39 |
| 2048 | 1.42 | 2.75 | 1.31 | 2.16 | 1.17 | 1.38 |

*Table XI.—Cinnamic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 5.°3. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 512 | 26.50 | 30.67 | 44.60 | 12.70 | 50.70 |
| 1024 | 36.40 | 42.11 | 61.22 | 17.40 | 69.63 |
| 2048 | 49.69 | 57.40 | 83.45 | 23.71 | 94.81 |

*Temperature Coefficients.*

| | 0°—5.°3. | | 5.°3—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 512 | 0.79 | 2.97 | 0.71 | 2.31 | 0.61 | 1.37 |
| 1024 | 1.08 | 2.96 | 0.97 | 2.30 | 0.84 | 1.37 |
| 2048 | 1.46 | 2.93 | 1.32 | 2.30 | 1.14 | 1.36 |

*Table XII.—o-Aminobenzoic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 7.5°. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 64 | 3.071 | 4.172 | 7.150 | 2.01 | 9.001 |
| 128 | 4.692 | 6.283 | 10.71 | 3.02 | 13.39 |
| 512 | 10.901 | 14.31 | 23.26 | 6.55 | 28.96 |
| 1024 | 16.03 | 20.48 | 33.53 | 9.45 | 41.57 |
| 2048 | 21.93 | 28.30 | 45.26 | 12.75 | 55.78 |

*Temperature Coefficients.*

| | 0°—7.°5. | | 7.°5—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 64 | 0.15 | 4.78 | 0.17 | 4.08 | 0.19 | 2.59 |
| 128 | 0.21 | 4.52 | 0.25 | 3.98 | 0.27 | 2.57 |
| 512 | 0.45 | 4.17 | 0.51 | 3.58 | 0.57 | 2.45 |
| 1024 | 0.65 | 4.03 | 0.72 | 3.46 | 0.81 | 2.40 |
| 2048 | 0.85 | 3.87 | 0.97 | 3.43 | 1.05 | 2.33 |

*Table XIII.*—p-*Aminobenzoic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 10.°19. | 25°. | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 64 | 3.711 | 5.136 | 7.370 | 2.08 | 8.919 |
| 128 | 5.346 | 7.527 | 10.84 | 3.05 | 12.97 |
| 512 | 12.57 | 17.39 | 24.54 | 6.91 | 29.06 |
| 1024 | 18.87 | 25.71 | 35.07 | 9.88 | 41.31 |
| 2048 | 28.32 | 37.21 | 50.13 | 14.12 | 58.56 |

*Temperature Coefficients.*

| | 0°—10.°19. | | 10.°19—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 64 | 0.14 | 3.78 | 0.15 | 2.92 | 0.16 | 2.10 |
| 128 | 0.21 | 4.00 | 0.22 | 2.97 | 0.21 | 1.96 |
| 512 | 0.47 | 3.76 | 0.48 | 2.78 | 0.45 | 1.84 |
| 1024 | 0.67 | 3.57 | 0.63 | 2.46 | 0.62 | 1.79 |
| 2048 | 0.87 | 3.08 | 0.87 | 2.35 | 0.84 | 1.68 |

*Table XIV.*—*Sulphanilic Acid. Molecular Conductivity and Dissociation.*

| | 0°. | 6.°3. | 25° | | 35°. |
|---|---|---|---|---|---|
| *V.* | $\mu_v$. | $\mu_v$. | $\mu_v$. | $\alpha$. | $\mu_v$. |
| 32 | 21.80 | 27.25 | 47.20 | 13.26 | 60.0 |
| 128 | 40.66 | 50.89 | 87.51 | 24.58 | 110.2 |
| 512 | 74.25 | 91.33 | 152.8 | 42.82 | 188.3 |
| 1024 | 96.40 | 118.1 | 193.0 | 54.23 | 237.0 |
| 2048 | 121.5 | 148.4 | 235.2 | 66.36 | 281.5 |

*Temperature Coefficients.*

| | 0°—6.°3. | | 6.°3—25°. | | 25°—35°. | |
|---|---|---|---|---|---|---|
| *V.* | Cond. units. | Per cent. | Cond. units. | Per cent. | Cond. units. | Per cent. |
| 32 | 0.88 | 4.03 | 1.07 | 3.91 | 1.28 | 2.71 |
| 128 | 1.62 | 3.99 | 1.96 | 3.85 | 2.27 | 2.59 |
| 512 | 2.71 | 3.65 | 3.29 | 3.60 | 3.55 | 2.33 |
| 1024 | 3.45 | 3.57 | 4.01 | 3.39 | 4.40 | 2.28 |
| 2048 | 4.27 | 3.52 | 4.53 | 3.06 | 4.63 | 1.97 |

Formic and oxalic acids are omitted from the list of acids investigated as it was found that they decompose in solution in the presence of the platinized electrodes. This decomposition proceeds so rapidly at high temperatures and dilutions

that there is no means of ascertaining when the solutions have come to constant conductivity. With formic acid it was noticed that constant readings could not be obtained within the short space of a few seconds, the conductivity falling off so rapidly. Conversion of the platinum black of the electrodes into platinum white, by heating in the flame of the blast lamp, lessened but did not entirely eliminate the trouble, so it was deemed best to leave the series of acids incomplete, rather than to give results which could not be absolutely relied upon. The same decomposition took place with gallic acid, but so slowly that good measurements were possible. The solution darkened when in contact with the electrodes, presumably owing to the formation of a small amount of pyrogallic acid, but the conductivity increased very gradually

The dissociation constants at 25°, calculated according to Ostwald's dilution formula,

$$K = \frac{\alpha^2}{v(1 - \alpha)},$$

are given in Table XV. No extended discussion on them seems necessary, as they are of the same order of magnitude as those obtained by Ostwald[1] in his comprehensive study of the affinity constants of organic acids at 25°. It is interesting to note the dilution at which the second hydrogen of the dibasic acids begins to dissociate. The dissociation constants of malonic, succinic and *o*-phthalic acids increase markedly from the dilution $V = 1024$ to that of $V = 2048$. It is therefore between these dilutions that the acidity of the acid increases. The results with these three acids compare very favorably with Ostwald's figures, and the constants for malonic and succinic acids agree satisfactorily with those of Walden.[2]

The increase with dilution in the values of the constants of *o*- and *p*-aminobenzoic acids should be noticed, and, as Ostwald[3] concluded, is probably caused by the breaking down of the inner salts on dilution. Further mention will be made of this fact.

[1] Z. physik. Chem., **3**, 170 (1889).
[2] *Ibid.*, **7**, 433 (1891).
[3] *Ibid.*, **3**, 261 (1889).

*Table XV.—Dissociation Constants* $\times 10^4$ *at 25°.*

| *V.* | Acetic acid. | Propionic acid. | Butyric acid. | Phenyl-acetic acid. | Malonic acid. | Succinic acid. | *o*-Phthalic acid. |
|---|---|---|---|---|---|---|---|
| 2 | 0.167 | 0.113 | 0.119 | ... | 15.9 | ... | .. |
| 8 | 0.180 | 0.135 | 0.151 | ... | 16.1 | 0.651 | .. |
| 32 | 0.181 | 0.137 | 0.157 | 0.517 | 15.9 | 0.662 | .. |
| 128 | 0.180 | 0.134 | 0.154 | 0.525 | 16.1 | 0.655 | 12.1 |
| 512 | 0.178 | 0.133 | 0.150 | 0.500 | 15.9 | 0.660 | 12.0 |
| 1024 | 0.177 | 0.129 | 0.149 | 0.498 | 16.1 | 0.661 | 12.1 |
| 2048 | 0.176 | 0.128 | 0.148 | 0.482 | 16.6 | 0.669 | 12.6 |

| *V.* | Benzoic acid. | Salicylic acid. | Gallic acid. | Cinnamic acid. | *o*-Amino-benzoic acid. | *p*-Amino-benzoic acid. | Sulphanilic acid. |
|---|---|---|---|---|---|---|---|
| 64 | 0.654 | 10.3 | 0.370 | ... | 0.647 | 0.688 | .. |
| 128 | 0.666 | 10.3 | 0.368 | ... | 0.740 | 0.752 | 6.26 |
| 512 | 0.662 | 10.2 | 0.416 | 0.359 | 0.897 | 0.100 | 6.26 |
| 1024 | 0.628 | 10.2 | 0.365 | 0.358 | 0.962 | 0.106 | 6.27 |
| 2048 | 0.617 | 9.5 | 0.366 | 0.360 | 0.910 | 0.113 | 6.29 |

Nearly all the acids investigated have temperature coefficients, expressed either in conductivity units or in percentages, which decrease with rise in temperature and with increase in dilution. This fact coincides with the theory of hydration of Jones referred to above. From the fact that in solutions containing metallic cations large temperature coefficients of conductivity are obtained, these coefficients being greatest in the most dilute solutions, it is clear that it is such ions which are largely hydrated in solutions. We should expect these large temperature coefficients if the ions are hydrated, since with rise in temperature the hydration would be greatly diminished and the velocity of the ions correspondingly increased; further, that the hydration would be greatest in dilute solutions where the mass action of the water comes most strongly into play, and thus rise in temperature produces a greater effect. With acids, however, there is probably not such enormous hydration. The temperature coefficients decrease regularly with dilution and rise in temperature and are generally small and of the same order of magnitude. The viscosity of the medium is the prime factor which influences increase in conductivity of acids with rise in temperature.

We turn to a fundamental part of the problem when we ask—

what function of the temperature is the conductivity of these acids? The results for each acid are shown graphically in Figures 1–4, in which conductivities are plotted as ordinates against temperatures as abscissae. It seems to be true generally that the conductivity of these organic acids is a *para-*

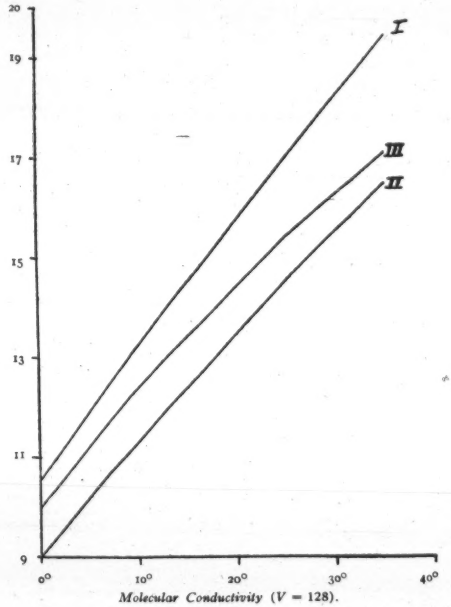


Fig. I.—I, Acetic acid; II, Propionic acid; III, Butyric acid.

*bolic* function of the temperature. The following table (XVI) gives values for $\mu_o$ and the constants $a$ and $b$ in the equation

$$\mu = \mu_o + at + bt^2,$$

where $\mu$ is the conductivity at any temperature $t$, $\mu_o$ the conductivity at 0°, $a$ and $b$ are constants dependent on the nature

of the acid. The dilution selected was N/128, and conductivities at 0°, 25° and 35° were used in obtaining the constants.

The last two columns of the table give values for the conductivities observed at the temperature $t$, and those calculated

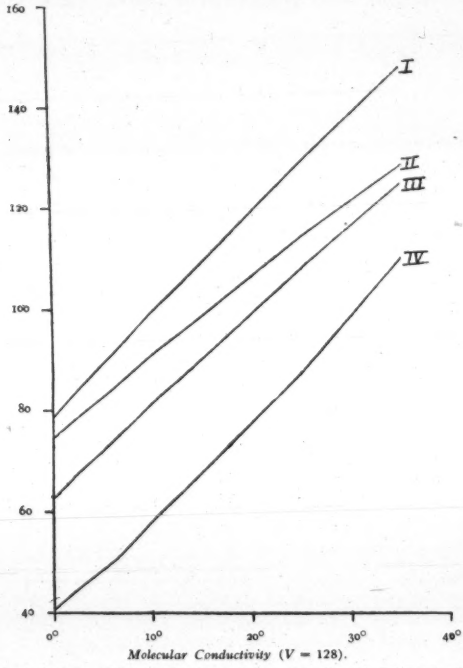


Fig. II.—I. Malonic acid; II. o-Phthalic acid; III. Salicylic acid; IV. Sulphanilic acid.

by the aid of the interpolation formulae. The agreement is seen to be satisfactory.

As exceptions to the statement made previously that acids have small temperature coefficients of conductivity, it is

noticed that sulphanilic acid, and *o*- and *p*-aminobenzoic acids have very large percentage temperature coefficients. This result is not due to hydrolysis, as the greatest effect would be evidenced in the most dilute solutions, whereas the

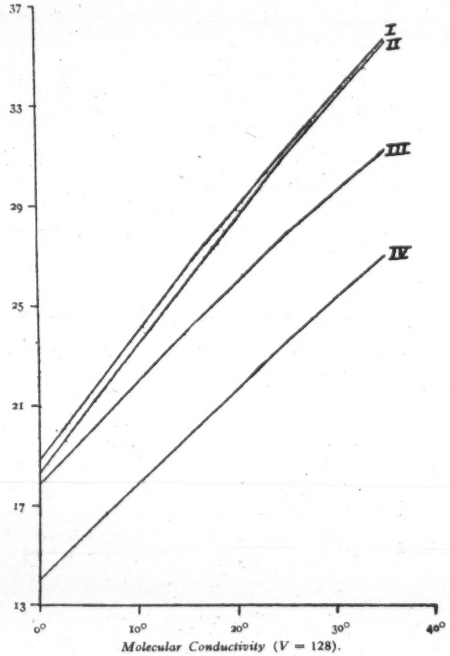


Fig. III.—I, Benzoic acid; II, Succinic acid; III, Phenylacetic acid; IV, Gallic acid.

temperature coefficients *decrease* with dilution. Also the conductivities of sulphanilic acid and *o*-aminobenzoic acid are not parabolic functions of the temperature. Here the temperature coefficients expressed in conductivity units increase

with rise in temperature, this increase being so great as to preclude conformity of behavior with the other acids. The probable cause of these discrepancies is to be found in the fact that these three acids form internal salts, having both basic and acidic groups. These internal salts would be broken down by rise in temperature, and the free acid would necessarily

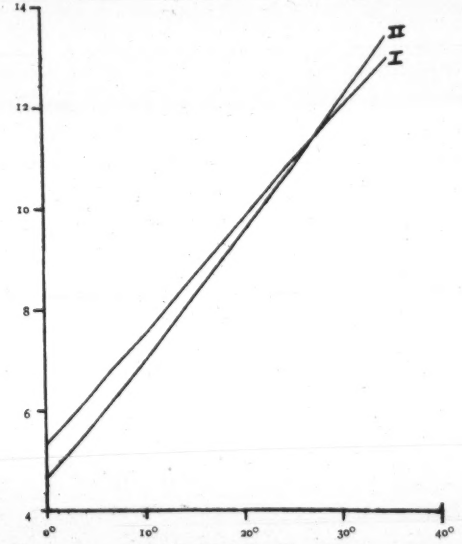


Fig. IV.—I, *p*-Aminobenzoic acid; II, *o*-Aminobenzoic acid.

conduct more than the salt itself. This theory is supported by the fact that *o*-aminobenzoic acid has much larger percentage temperature coefficients than the para acid, and also that the coefficients in conductivity units increase largely with the temperature, in consequence of the greater tendency of the ortho acid (whose salt-forming groups are nearer to-

gether in space) to form an internal salt. This point will be further tested by a study of other amino acids. This work is being continued in this laboratory.

*Table XVI.*

| Acid. | $\mu_0$. | *a*. | *b*. | *t*. | $\mu_t$ obs. | $\mu_t$ calc. |
|---|---|---|---|---|---|---|
| Acetic | 10.48 | 0.287 | —0.000856 | 9.°2 | 13.04 | 13.05 |
| Propionic | 9.00 | 0.244 | —0.000856 | 6.°9 | 10.60 | 10.64 |
| Butyric | 10.00 | 0.253 | —0.00140 | 9.°4 | 12.23 | 12.26 |
| Phenylacetic | 17.82 | 0.460 | —0.00217 | 13.°25 | 23.39 | 23.44 |
| Malonic | 78.30 | 2.217 | —0.00628 | 4.°9 | 88.83 | 89.00 |
| Succinic | 18.24 | 0.567 | —0.00184 | 5.°7 | 21.35 | 21.40 |
| *o*-Phthalic | 74.56 | 1.752 | —0.00571 | 8.°23 | 88.32 | 88.58 |
| Benzoic | 18.79 | 0.556 | —0.00207 | 15.°8 | 26.93 | 27.04 |
| Salicylic | 62.65 | 1.919 | —0.00411 | 6.°9 | 75.59 | 75.68 |
| Gallic | 14.01 | 0.408 | —0.000982 | 6.°5 | 16.55 | 16.62 |
| *p*-Aminobenzoic | 5.35 | 0.215 | —0.000189 | 10.°19 | 7.53 | 7.52 |

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV., October, 1909.

## REPORT.

### RECENT PROGRESS IN OUR KNOWLEDGE OF THE RADIOACTIVE ELEMENTS.

#### *I. Radioactive Radiations.*

Radioactive substances are detected by means of the radiations which they emit. This property of emitting radiations is a very important one and through it our knowledge of the internal structure of the atom has been greatly increased. The various radiations are of four kinds, the $\alpha$-, $\beta$-, and $\delta$-particles, and the $\gamma$-rays.

The $\alpha$-particles consist of positively charged bodies of atomic size moving with a velocity almost as great as that of light, 300,000 kilometers per second. They are very similar to the positive carriers found in anode and canal rays. The $\beta$-particles are very swiftly moving negative electrons. The $\alpha$- and $\beta$-particles possess such a great velocity that they produce intense ionization when passing through a gas. On the other hand, the $\delta$-particles move at the rate of only about $3.3\ (10)^{-8}$ cm. per second and do not ionize the gas through which they pass. The $\gamma$-rays are very similar to X-rays and cannot be deflected by electric or magnetic fields. This shows

that the $\gamma$-rays consist, not of charged particles, but either of uncharged particles or of electromagnetic pulses.

### *II. The $\alpha$-Particles.*

The absorption of the various radiations appears to be due mainly to two causes: loss of energy, which produces a gradual loss of speed, and scattering, which brings about a diminution in the number of particles in the primary beam. The $\beta$-particles, being very small, are believed to penetrate atoms lying in their path. As they are easily deflected by electric and magnetic fields, the intense fields within the atoms make their path very irregular. For this reason the problem of tracing the history of a $\beta$-particle is very complex and beset with many difficulties, owing largely to our ignorance of the structure of an atom. The $\alpha$-particle, however, is of atomic size so that while its velocity is very great, it pursues practically a rectilinear course. This makes the study of the motion of an individual $\alpha$-particle comparatively simple.

Rutherford and others have found that all $\alpha$-particles are emitted by any radioactive product at the same velocity and that the $\alpha$-particles from various radioactive products differ only in their velocity of ejection. In passing through matter their velocity decreases and when it falls below a certain critical value, $0.82\ (10)^9$ cm. per second,[1] the particles cease to ionize the air, to affect the photographic plate, or to produce phosphorescence. The distance which the $\alpha$-particle will traverse in air under standard conditions of pressure and temperature is known as its range. The range of the $\alpha$-particle is an important constant for any radioactive product. It differs for $\alpha$-particles coming from different radioactive products. Rutherford gives an empirical formula,

$$V = 0.348\ V_0\ \sqrt{r + 1.35},$$

by means of which we can calculate the velocity $V$ of an $\alpha$-particle for any point in its path if we know the range. $V_0$ is the initial velocity of the $\alpha$-particle emitted by radium C and is equal to $2.06\ (10)^9$ cm. per second, and $r$ is the remaining part of the range which the $\alpha$-particle has yet to traverse from the point in its path which is being considered.

Recently Duane[2] has attacked the problem as to whether an $\alpha$-particle loses its charge at the same time that it ceases to ionize the surrounding gas. His conclusion is that it does. The $\alpha$-particles, when they impinge upon a solid body, pro-

[1] Rutherford: Phil. Mag., **12**, 140 (1906). Lerch: Z. Elek. Chem., **13**, 381 (1907).
[2] Am. J. Sci., **26**, Nov. (1908).

duce $\delta$-particles at its surface. Duane finds that beyond their range the $\alpha$-particles cease to produce these secondary $\delta$-particles. At present, therefore, we have no means of detecting the $\alpha$-particle when its velocity is less than $1.8\ (10)^9$ cm. per second, so that if any element emits $\alpha$-particles with a velocity less than this, there is no direct method of discovering it.

It has been known for some time that helium accumulates in radium, actinium, and thorium compounds and it has often been suggested that this helium consists of the $\alpha$-particles after they have lost their charge. But this is difficult to prove. The value of $e/m$ ($e$ being the charge and $m$ the mass) is known for the $\alpha$-particle. If $e$ could be measured, $m$ could be determined and if its value should come out about the same as that for the helium atom, the evidence that the $\alpha$-particle is simply a charged helium atom moving with a very great velocity would be very strong. Now it is possible to find the charge which a beam of $\alpha$-particles will carry to a plate. If the number of carriers could be counted, then $e$ could be calculated and $m$ determined from the known ratio $e/m$. $\alpha$-Particles striking upon a zinc sulphide screen produce scintillations which can easily be seen and Regener[1] has used this method for counting the $\alpha$-particles, each $\alpha$-particle being supposed to strike the zinc sulphide and to produce a scintillation. Rutheford and Geiger[2] have recently attained the same object in a very ingenious manner by magnifying the ionizing power of the $\alpha$-particles. Notwithstanding its enormous power to ionize gases, an $\alpha$-particle entering an ionization chamber would not produce enough ions in the gas to give rise to a current that could be easily detected. Townsend[3] has worked out the conditions under which ions can be formed by collision between neutral gas molecules and ions moving in a strong electric field. Suppose that the current between parallel plates immersed in a gas at low pressures is observed when the air is ionized by X-rays. In a weak field the current increases with the voltage and soon reaches a constant value, the saturation current. If the field is increased beyond a certain point, however, the current rises rapidly and Townsend showed that this was due to the production of fresh ions in the gas by the collision of negative ions with the gas molecules. Under such conditions the small current through the gas due to an external ionizing agency may be increased hundreds or even thousands of

[1] Ber. d. physik. Ges., **10,** 78 (1908).
[2] P. Roy. Soc., A. **81,** 141.
[3] Phil. Mag., Feb., 1901; Jan., 1902; Apr., Sept. and Nov., 1903.

times. Rutherford and Geiger place their charged plates near a small opening from which α-particles are emerging. As an α-particle enters the electric field between the plates it produces ions by collision, and these ions are given sufficient velocity by the electric field to produce other ions by collision with the neutral gas molecules. The result is that sufficient current is produced between the plates to cause a kick in the electrometer needle. In this way the α-particles can easily be counted.

Rutherford and Geiger found that the number of α-particles entering the opening, and also the interval between successive throws of the electrometer, varied within quite wide limits. This is to be expected from the theory of probability, upon which the present kinetic theory of gases is based. The α-particles from uranium, thorium, radium and actinium compounds have been counted by Rutherford and Geiger, who believe that this method of automatic increase of ionization by collision can be used to extend very considerably the range of measurement of minute quantities of radioactive matter and that under good conditions the β-particles can be counted in the same way. They found for a given intensity of radiation that the number of α-particles entering the detecting vessel varied as the area of the aperture and that for radium C the α-particles are projected equally in all directions. As an example of their results the following table is given. $Q_o$ is the number of α-particles expelled per second per gram of radium. After making a correction, the value $3.4\ (10)^{10}$ is taken for $Q_o$:

*Table I.*

| Gas. | Pressure in detecting vessel. | Voltage. | Diameter of aperture. | Number of throws of electrometer. | $Q_o$. |
|---|---|---|---|---|---|
| Air | 3.75 | 1200 | 1.23 | 161 | $3.20\ (10)^{10}$ |
| $CO_2$ | 4.8 | 1360 | 1.23 | 59 | $3.10\ (10)^{10}$ |
| $CO_2$ | 4.8 | 1360 | 1.23 | 118 | $3.30\ (10)^{10}$ |
| $CO_2$ | 4.2 | 1320 | 1.92 | 194 | $3.43\ (10)^{10}$ |

From experiments of Bragg and Boltwood it appears very probable that the same number of α-particles is expelled per second from radium and each of the α-ray products in equilibrium with it. This is also supported by the fact that radium, the radium emanation, radium A, and radium C each produce about the same amount of ionization when the four products are in equilibrium. This is not true of all the radioactive elements, however. Bronson[1] finds evidence that an

[1] Phil. Mag., Aug., 1908.

atom of thorium C, in breaking up, gives off the same number of $\alpha$-particles as an atom of thorium B and that an atom of the thorium emanation gives off four times this number; also that an atom of actinium emanation, in breaking up, gives off twice as many $\alpha$-particles as an atom of its active deposit. Rutherford and Geiger[1] assume that each atom of the $\alpha$-ray products of radium ejects one $\alpha$-particle when it breaks down. As there are four radium products which emit $\alpha$-particles, it would follow that the number of $\alpha$-particles emitted per second per gram of radium in equilibrium is $4 \times 3.4\ (10)^{10}$ and that in one gram of radium, $3.4\ (10)^{10}$ radium atoms break up per second.

Knowing the number of $\alpha$-particles produced per second by radium and measuring the total charge which they carry, we get the charge on each particle. Rutherford and Geiger[1] allow the charge to accumulate on an insulated plate exposed to one of the active products. The whole is placed in a very good vacuum to prevent any loss of charge by a current through ionized gas. It is also necessary to use a strong magnetic field, for the $\alpha$-particles, in passing through matter, lib rate a large number of $\delta$-particles. In a moderately strong field the $\delta$-particles describe very small orbits and return to the surface from which they were emitted. The field also deflects any $\beta$-particles that might otherwise charge the insulated plate. The result of Rutherford and Geiger's work is to show that $E$, the charge on the $\alpha$-particle, is $9.3\ (10)^{-10}$ electrostatic units. From calculations based upon the heating effect of radium and where it is assumed that this is due to the kinetic energy of the $\alpha$-particles, the value $9.1\ (10)^{-10}$ electrostatic units for $E$ is obtained.

Using the results of their experiments, Rutherford and Geiger calculate the value of the following quantities:

*Table II.*

$E$ (charge on an $\alpha$-particle) $= 9.3\ (10)^{-10}$ electrostatic units.
$e$ (charge on a negative corpuscle) $= 4.65\ (10)^{-10}$ electrostatic units.
Atoms in one gram hydrogen $= 6.2\ (10)^{23}$.
Mass of hydrogen atom $= 1.6\ (10)^{-24}$ gram.
Avogadro's constant $= 2.72\ (10)^{19}$.
$E/M$ ($M$ is mass of $\alpha$-particle) $= 5.07\ (10)^{3}$ electromagnetic units.
$M = 3.84$.
Mass of helium atom $= 3.96$.

[1] P. Roy. Soc., A. **81**, 141, etc.

Number of atoms of radium breaking up per gram per second = $3.4\ (10)^{10}$.
Volume of radium emanation produced per second per gram radium = $1.25\ (10)^{-9}$ cc.
Volume of radium emanation in equilibrium with one gram radium = 0.585 cubic mm.
Amount of helium produced per gram radium per day = 0.43 cubic mm.
Calculated heating effect of one gram radium = 113 gram cal. per hour.
Calculated half-period of radium = 1750 years.

Some of these values have recently been verified by other experimenters. In the electrolysis of a monovalent salt, 96550 coulombs are carried by $N$ atoms, so that

$$N e = 3\ (10)^9 \times 96550 \text{ electrostatic units.}$$

Applying the gas laws to emulsions, Perrin[1] finds $N = 71\ (10)^{22}$ and $e = 4.1\ (10)^{-10}$. Quite recently Millikan[2] has repeated the Thomson-Wilson determination of $e$ and obtains a mean value of $4.65\ (10)^{-10}$ electrostatic units. He caused expansion clouds to be formed in alcohol as well as in water. He finds that many of the droplets have several—some as high as six—charges on them. Boltwood[3] finds the half-period value of radium to be about 2000 years, the experimental error being such as to make his results too large. In any series of successive disintegrating radio products, A, B, C, etc., in equilibrium, the number of atoms of the parent substance disintegrating per second is equal to the number of atoms of each successive product disintegrating per second. Let $\lambda_1$, $\lambda_2$, $\lambda_3$, etc., be the respective fractions of the total amounts of each product which undergo change each second. Then $\lambda_1 A_1 = \lambda_2 B_2 = \lambda_3 C_3$, etc., where $A_1$, $B_2$, etc., are the number of atoms of $A$, $B$, etc., present. Since radium decays so slowly it is difficult to find its rate of disintegration. If, however, the parent substance (A) from which radium is formed can be separated from a primary uranium mineral (where the age is certainly sufficient for radioactive equilibrium to have been reached), and the amount ($\lambda_1$) of radium produced by this parent can be determined and compared directly with the amount ($B_2$) of radium with which it was associated in the mineral, it is possible to get quite an accurate value for the constant ($\lambda_2$) of change of radium. Boltwood

[1] Compt. Rend., **147**, 594 (1908).
[2] Report before Am. Phys. Soc., Oct. 23, 1909.
[3] Am. J. Sci., June, 1908.

separated out ionium ($A_1$) from uranium minerals. He found the amount of radium in equilibrium with this ionium and also the rate ($\lambda_1$) of production of radium from ionium. Five solutions of ionium were used. As a result he found

$$\lambda_2 = \frac{\lambda_1 A_1}{B_2} = 2000 \text{ years for the half-period value.}$$

Dewar[1] has made a series of measurements of the rate of production of helium from radium which agrees very well with the above value, calculated upon the assumption that the $\alpha$-particles are charged helium atoms. He used the 70 mg. of very pure radium chloride with which Thorpe[2] had determined the atomic weight of radium. By using a radiometer he was able to detect increases of helium in quantities as small as that produced from 10 mg. of radium bromide in a few hours. He finds that 0.37 cubic mm. of helium accumulates in 1 gram of radium per day. This agrees very well with the calculated value.

The above evidence then is very strong that the $\alpha$-particle is a charged helium atom. In addition Rutherford and Royds[3] have shown that helium can be obtained from accumulated $\alpha$-particles, quite independently of the active matter from which they are expelled.

From these discoveries concerning the nature of the $\alpha$-particle it must be concluded that the atoms of known radioactive elements are in part made up of helium atoms, which are liberated at definite stages during the disintegration. We also know that these radioactive elements contain several $\beta$-particles. J. J. Thomson,[4] in a very important paper, shows by three entirely independent methods that the number of $\beta$-particles in the atom of any element is about the same as the number representing its atomic weight. The helium atom would then contain at least four corpuscles.

The above results[5] can be used to calculate the atomic weights of various radioactive products. In the uranium-radium series are several $\beta$-ray and rayless products. Assuming that no mass comparable in size to the hydrogen atom is expelled under these conditions and taking the atomic weight of helium as 4, we have: Uranium, 238.5; uranium X, 234.5; ionium, 230.5; radium, 226.5; emanation, 222.5; radium A, 218.5; radium B, 218.5; radium C, 214.5; radium D, E, and F (radio-lead), 210.5; polonium, 210.5; final prod-

[1] P. Roy. Soc., A. **81**, 280.
[2] *Ibid.*, **80**, 298.
[3] Nature, **1908**, 119; Phil. Mag., **98**, 281 (1909).
[4] Phil. Mag., June, 1906.
[5] Nature, Nov. 5, 1908.

uct, lead, 206.5. These values are in good agreement with those determined experimentally. Madame Curie[1] gives the value 226.2 as the atomic weight of radium; Thorpe,[2] 226.7. The atomic weight of lead is 206.8. Perkin[3] obtains about 235 at the atomic weight of the radium emanation. [This value is in good agreement with the calculated value, considering the great experimental difficulties met with in this kind of work. Previous investigators had obtained very discordant results for the atomic weight of radium emanation. In applying Graham's law, that the molecular weights of two gases are inversely proportional to the squares of their coefficients of diffusion, it is necessary to use gases of the same order of molecular weight. For this reason Perkins used mercury vapor. This and the radium emanation resemble each other very much and both are believed to be monatomic.]

On account of the small mass of the electron its expulsion from an atom does not produce any very great rebound of the atom. But when an $\alpha$-particle is ejected, the rebound causes the atom to move with a very considerable velocity in the opposite direction to that of the $\alpha$-particle. A study of these atomic motions has recently been made by Russ and Makower.[4] They find the absorption in air and hydrogen to be an exponential function of the pressure. When an active deposit exists on a solid and is emitting $\alpha$-rays, it also emits some of its disintegrated atoms.

All experimental evidence indicates that the $\alpha$-particles from the different radioactive substances are identical in mass and charge and differ only in their initial velocity. They cease to ionize when their velocity falls below $1.5\ (10)^9$ cm. per second. No simple relation has been found between ionization and the velocity of the $\alpha$-particles. Geiger[5] gives the following numbers for the ions produced by an $\alpha$-particle from the various radium products:

| | Range. | Total number ions produced. |
|---|---|---|
| Radium | 3.50 | $1.53\ (10)^5$ |
| Emanation | 4.33 | $1.74\ (10)^5$ |
| Radium A | 4.83 | $1.87\ (10)^5$ |
| Radium C | 7.06 | $2.37\ (10)^5$ |
| Radium F | 3.86 | $1.62\ (10)^5$ |

[1] Compt. Rend., **145**, 422 (1907).
[2] P. Roy. Soc., A, **80**, 529.
[3] Am. J. Sci., June, 1908.
[4] Physik. Z., June, 1909.
[5] P. Roy. Soc., A, **83**, 486 (1909).

### *III. The β- and γ-Radiations.*

It has been known for some time that $\beta$-radiations consist of negative corpuscles moving with very great velocities. One of the most important experiments ever made concerning the nature of matter was that of Kaufmann in which he found that the value of $e/m$ depends upon the velocity of the corpuscle. If $e$ is constant this would mean that $m$ increases with the velocity. Assuming that the corpuscle is a sphere of radius $a$ and that it has a charge $e$ at its center, Thomson found that Kaufmann's results agreed with calculated values. In this way all the inertia of the corpuscle could be accounted for by its charge and the estimated value of $a$ ($10^{-13}$ cm.). Recent experiments of Bucherer[1] are also very important in that they give very strong evidence to support the Lorentz-Einstein[2] theory of relativity.

The fundamental facts of optics and electrodynamics, the aberration of the stars, and many other phenomena indicate that the ether does not take part to any sensible extent[3] in the motion of material bodies that are moving through it. The theory of a stagnant ether would lead us to expect a positive result in the celebrated experiments of Michelson and Morley. An explanation of these experiments was given in 1892 by Lorentz. According to his theory, in any material body moving relatively to the ether all of its dimensions in this direction are decreased by the ratio $\sqrt{1 - \frac{v^2}{V^2}}$ to 1, the directions perpendicular to the motion remaining unchanged. (This contraction is very small and for the earth's diameter in the direction of its orbital motion is 6.5 cm.) $V$ is the velocity of light, and $v$ the velocity of the body with reference to the ether about it. According to the Lorentz theory, an electron at rest is a sphere of radius $a$, in motion an ellipsoid of revolution with its shorter axis in the direction of motion and equal to $a\sqrt{1 - \frac{v^2}{V^2}}$. Using the Lorentz theory, Bucherer finds that $e/m_0$ for the $\beta$-particle from radium is $1.730\ (10)^7$, where $m_0$ is the mass of the particle at rest.

Considerable work has been done recently on the absorption of $\beta$-rays and the secondary radiations which they excite. McClelland[4] finds that the secondary radiation con-

[1] Physik. Z., Nov. 1, 1908.

[2] Lorentz: Versuch einer Theorie der elektrischen und optischen Erscheinungen, in bewegten Körpern, Secs. 68, 89, etc. Einstein: Ann. Phys., **17**, 891 (1905).

[3] J. J. Thomson: Physik. Z., Aug. 15, 1908.

[4] P. Roy. Soc., A, **80**, 501.

sists partly of reflected primary rays and partly of corpuscles which appear to have been expelled from the atoms when disturbed by the entry of the primary rays. The relative intensity of the secondary radiation depends directly upon the atomic weight of the element upon which the primary rays fall. Regener[1] finds that $\beta$-rays produce scintillations when they strike upon a screen of barium platinocyanide between 10 and 50 cms. from the source. Wilson[2] shows that the absorption by matter of homogenous $\beta$-rays, measured by the ionization, does not take place according to an exponential law, but according to a law which is practically linear.

The rays emitted by uranium X, radium E and actinium are heterogenous. The $\alpha$-particles lose energy gradually as they pass through matter and finally cease to be effective as ionizing agents. In contrast to this method of absorption Schmidt,[3] McClelland and Hackett,[4] Makower[5] and others assume that the $\beta$-particles are stopped in mid-career while their velocity is still high.

Makower[5] finds that $5.0\ (10)^{10}$ $\beta$-particles are emitted per second by the radium C in radioactive equilibrium with one gram of radium.

Investigations on $\gamma$-rays are leading more and more to the view[6] that these rays are practically identical with X-rays, the most notable difference being that $\gamma$-rays originate from the same source as the $\beta$-rays, whereas X-rays start where cathode rays are stopped.

The nature of X- and $\gamma$-rays has been very much discussed recently. According to the theory of Stokes, these rays consist of ether pulses of intense electric and magnetic forces perpendicular to each other and to the direction of motion (as in light). The ionization produced by the rays represents the effect of the electric force in the wave front, causing the ejection of electrons from atoms which it encounters. The ionizing effect of ultraviolet light differs then only in degree from that of $\gamma$-rays. Since only a few molecules (one in a billion when the radiation is intense) are ionized, Thomson[7] believes that ether pulses and waves are localized in limited regions, the wave front possessing a structure similar

[1] Ber. d. physik. Ges., **10,** 351 (1908).
[2] P. Roy. Soc., A, **82,** 612.
[3] Jahrb. der Rad., 1908.
[4] Trans. Roy. Soc., Dubl., Vol. 9, No. 4 (1907).
[5] Phil. Mag., January, 1909.
[6] Eve: Phil. Mag., Aug., 1908.
[7] P. Phil. Soc., Camb., **14,** 417 (1907).

to bright specks on a dark background. This implies a structure in the ether, which is assumed to have discrete lines disseminated through it. $\gamma$-Rays would then simply be pulses along these lines or threads.

Bragg[1] suggests that X- and $\gamma$-rays consist of a close association of positive and negative particles which rotate about each other. He believes the negative particle to be the negative electron and suggests that the positive particle may be the "positive" electron (not isolated as yet). The penetrating power would depend upon the distance between the components of the pair. The discontinuous pulse and the neutral pair theories are so much alike that present experimental evidence does not allow us to discriminate between them.

Madsen[2] finds the $\gamma$-rays of radium and possibly of thorium to consist of two distinct homogenous bundles. Secondary $\gamma$-radiation appears on both sides of a plate penetrated by a stream of $\gamma$-rays. The amount of secondary radiation from the two sides differs very much. Eve[3] concludes that a change of hardness of the $\gamma$-rays makes but little difference upon the relative intensities of the incident secondary corpuscular radiation, and the intensities follow the order of the atomic weight of the radiators. A change in hardness of the $\gamma$-rays makes a marked difference in the relative intensities of the emergent corpuscular secondary radiation from various elements. These secondary radiations do not follow the order of atomic weight.

### *IV. Temperature Coefficient in Radioactive Changes.*

The theory proposed by Rutherford and Soddy to explain the behavior of radioactive changes assumes that the phenomena of radioactivity are accompanied by the disintegration of the atoms of the radio-elements and the production of other elements having distinctive physical and chemical properties. These transformations would therefore be very different from ordinary chemical reactions where the atoms all retain their identity throughout the changes.

An interesting and very important problem which has engaged the attention of several experimenters is whether temperature or pressure change the rate of decay of any radioactive products. This would have an important bearing in geology where radioactive minerals must be considered

[1] Trans. Roy. Soc. South Australia, **31,** 79 (1907); Phil. Mag., Oct., 1907; Nature, Jan. 23, Apr. 16, July 23, July 30, 1908.

[2] Phil. Mag., **1909,** 423.

[3] *Ibid.*, **1909,** 275.

as subject to enormous pressures and high temperatures. Schuster found that the activity of the radium emanation, when subjected for four days to a pressure of 2000 atmospheres, was not changed. Eve showed that a pressure of 20,000 atmospheres did not affect the rate of decay of radium C. Quite a large number of investigators have tried the effect of changing the temperature of the radioactive product. Engler[1] claims that radioactive changes have a temperature coefficient. Schmidt and Cermak,[2] however, do not find any temperature coefficient for radium C up to 1500° C. and this was one of the products used by Engler. Forsyth[3] concludes that the rate of production of uranium X at 1000° C. is not sensibly different from that at ordinary temperatures. All the results agree in this, that if there is any temperature coefficient at all, it is very small.

One of the enigmas at present is the source of the sun's heat. It has been shown by Newcomb and others that the theory of contraction as expounded by Helmholtz is insufficient to account for the energy the sun loses by radiation. At present, then, no suitable source is known. It has been suggested by Anderson that some elements may be "radioactive" at high temperatures that are not at low temperatures. Our present knowledge of radioactivity, however, does not seem to indicate this. It is very important that experiments along this line should be made.

*V. Properties and Distribution of the Radium Emanation.*

Radium emanation, on account of its comparatively long period of decay (half-period value, 3.75 days), is being more thoroughly studied than any of the other products of radioactive transformation. Ramsay and Cameron[4] found 7.07 cubic mm. of emanation in equilibrium with one gram of radium. As this value is much higher than that obtained by calculation, Rutherford[5] considers that either the assumptions made in the calculations are wrong or Ramsay and Cameron's result is too high.

The emanation is driven from the radium either by heating (830° C.) or by solution. It is then kept over potassium hydroxide for several hours to absorb the carbon dioxide. On cooling the emanation to the temperature of liquid air it will condense and any volatile gases mixed with it can be pumped

[1] Ann. Phys., **1908**, 483.
[2] Physik. Z., Nov. 15, 1908.
[3] Phil. Mag., **1909**, 207.
[4] J. Chem. Soc., **1907**, 1593.
[5] Phil. Mag., Aug., 1908.

off. The purity of the emanation was examined spectroscopically.[1] The emanation spectrum in the discharge tube entirely disappeared when the tube was cooled below the liquefying point of the emanation. Ramsay and Cameron[2] found a very rapid decrease of volume when the emanation was removed from the radium and a more gradual decrease afterwards. Rutherford found a general decrease in volume but did not observe the sudden initial decrease. The emanation obeys Boyle's law.

Rutherford's results, which follow, are in fairly good agreement with the calculated value (0.58 cubic mm.):

| | Initial volume of emanation per gram radium. | Final volume of emanation per gram radium. |
|---|---|---|
| Experiment II | 1.32 | 0.59 |
| " III | 0.80 | .... |
| " IV | 0.97 | 0.66 |
| " V | 1.05 | 0.58 |

Cameron and Ramsay[3] state in their work on the radium emanation that it was extremely difficult to prevent traces of air from leaking into their apparatus during the considerable time which must elapse before an experiment is completed. One-tenth cc. of air contains sufficient argon to be detected spectroscopically and they consider the proof of the formation of argon as being very difficult. On account of the wide distribution of lithium, they also consider it far from easy to prove that lithium did not pre-exist in the solution. But, according to them, the detection of neon is not open to any such objection. Mme. Curie and Mlle. Gleditsch[4] have repeated the experiments with reference to the transformation of copper into lithium when a copper solution is acted upon by radium emanation and they have obtained no evidence of the production of lithium. Strutt[5] has shown that the presence of neon can be shown spectroscopically in 0.1 cc. of air, and as Cameron and Ramsay state, it is very hard to avoid a small air leakage in apparatus that is used for a week or more. Rutherford[6] has repeated their experiments on the action of radium emanation upon a pure water solution.

In preliminary experiments Rutherford found it possible to detect the yellow neon line when $^1/_{15}$ cc. of air was intro-

[1] Rutherford and Royds: Phil. Mag., Aug., 1908.
[2] *Loc. cit.*
[3] J. Chem. Soc., **1908,** 992.
[4] Compt. Rend., **147,** 345 (1908); THIS JOURNAL, **40,** 485 (1908).
[5] P. Roy. Soc., A, **80,** 572 (1908).
[6] Phil. Mag., Nov., 1908.

duced into his apparatus, with $^2/_{15}$ cc. the red lines of neon flashed out, and with $^2/_{10}$ cc. of air a brilliant spectrum of neon was obtained. Experiments similar to those of Cameron and Ramsay were carried out. The residual gas was much smaller in amount than that obtained by Cameron and Ramsay and showed a brilliant spectrum of helium but not a trace of neon. The presence of neon found by Cameron and Ramsay is therefore most likely due to a small leakage of air into their vessel. In the above experiments the use of cocoanut charcoal (cooled with liquid air) to absorb all gases except helium and neon is every essential.

Elster and Geitel found that when a negatively charged wire is exposed in the air a radioactive deposit of radium and thorium is formed upon it. From experiments of this kind it was inferred that the radium emanation was present in the air, coming probably from the ground, which is known to contain a small quantity of radium. The first to make a direct quantitative measurement of the radium emanation in the atmosphere was Eve.[1]

A known quantity of air is passed over cocoanut charcoal in glass tubes. The charcoal absorbs the emanation which is afterwards driven off by heating and measured with an electroscope. One cubic meter of air at Montreal was found to contain an amount of emanation equal to that corresponding to $40\,(10)^{-12}$ gram of radium when in equilibrium with it. Ashman,[2] at Chicago, collected the emanation by passing air through vessels cooled with liquid air, the emanation condensing on the sides of the vessels. The amount of emanation in the air varied with the weather conditions, ranging between the values $86\,(10)^{-12}$ and $200\,(10)^{-12}$. Satterly,[3] at Cambridge (England), used the charcoal and liquid air methods and obtained the value $100\,(10)^{-12}$ for the amount of emanation. This amount of emanation, together with the disintegration products, would produce about 3 ions per cc. per second. As the number of ions produced in air is ten times this amount, it follows that only a small proportion of the natural ionization of the air is due to the presence of radium emanation and its products. Eve[3] gets maximum values for the amount of emanation in the air when there are well-defined cyclones accompanied by heavy rains or a quick thaw of snow. Anticyclones with dry weather and very low temperatures in winter give minimum values. The average amount at Montreal in a year is $60\,(10)^{-12}$, the amount vary-

[1] Phil. Mag., Dec., 1907.
[2] Am. J. Sci., Aug., 1908.
[3] Phil. Mag., Oct., 1908.

ing so that the maximum was to the minimum as seven to one. The writer[1] has found the penetrating radiation to be small under anticyclonic conditions.

*VI. Radioactivity of the Ordinary Elements.*

Ever since the discovery of the radioactivity of uranium investigations have been made to determine if any of the other elements are radioactive. The conclusion of most of the experimenters is that they are not.

A gas in a closed vessel is slightly ionized and this ionization is partly due to the walls of the vessel. By using vessels of the same size and shape and containing the same gas, it is found that the ionization is different for different metals and at first it was considered that this was evidence that ordinary metals are active. But different samples of the same metal cause different amounts of ionization. Lead usually possesses considerable ionizing power. McClennan[2] has tested quite a large number of different specimens of lead. He measured the ionization in a cylinder of the given metal 60 cm. long and 24 cm. in diameter. The number of ions produced per second per cc. for different specimens of lead varied between 160 and 23. Zinc and aluminium each gave 15. It has been known for some time that there is a very penetrating radiation which, like the $\gamma$-rays from radium, makes it necessary to place lead screens several cm. thick about an ionization chamber before it is entirely absorbed. McClennan believes that in the case of aluminium, zinc, and the one sample of lead (23-ion case), the ionizing power was due to this penetrating radiation and secondary radiations excited by it. It is probable that the other samples of lead contain some radioactive impurity. Elster and Geitel[3] have been able to extract from some specimens of lead a radioactive substance which resembles radium F.

Greinacher[4] and Serviss[5] have examined several metals for a possible temperature gradient. An element might be radioactive and eject $\alpha$-particles with a velocity less than that required to produce ionization. It would at present be impossible to detect such radiations directly.

In a solid, however, they would soon be stopped and their kinetic energy transformed into heat. The inside of a cylinder made of such a substance would be warmer than the out-

[1] Phys. Rev., June and July, 1908.
[2] Phil. Mag., Dec., 1907.
[3] Physik. Z., Nov., 1906.
[4] Ann. Phys., **1907**, 79.
[5] Am. J. Sci., Dec., 1907.

side. Very careful measurements have thus far failed to show any such temperature gradient for the ordinary metals.

Campbell and Wood[1] and Wood[2] have shown that potassium and rubidium salts emit ionizing rays similar to the $\beta$-rays of uranium. They estimated the activity of potassium to be about one-thousandth that of uranium. Levin and Ruer[3] have investigated various potassium salts photographically and corroborate Wood and Campbell's results. McClennan and Kennedy[4] have made a more detailed investigation, measuring the saturation current when different salts are spread in uniform layers and placed in an ionization chamber. The activity, as measured by the saturation current, varied directly as the area of the salt exposed. It increased as the thickness of the salt layer was increased until this reached 2.5 mm. when the current became constant. Thirty-five potassium salts were tried. All showed a considerable activity. Lithium, sodium, and ammonium salts showed no activity, caesium and rubidium salts only a very slight amount. Fifteen cm. of air reduced the ionization to half value. The mean value of the absorption constant $\lambda$ for tin foil was about 125, the value decreasing as the thickness of foil was increased, showing that the rays were not homogenous. Experiments showed that the $\beta$-like radiations were not secondary radiations excited by a penetrating radiation such as the $\gamma$-rays from radium, for potassium salts do not give rise to any greater proportion of secondary radiation than other salts when exposed to $\gamma$-rays. Henriot and Vavon[5] attempted to concentrate the radioactivity of potassium salts by fractional methods, but with no success. Campbell showed that the $\beta$-rays from potassium salts can be deviated by an electric field. Henriot and Vavon deflected the rays with a magnetic field, and the deflection was in such a direction as to indicate that they are negatively charged. Strong[6] found that various potassium, rubidium and erbium salts are radioactive.

If subatomic changes go on in the atoms of the ordinary elements and $\alpha$-like particles are ejected, then it would be expected that minerals of these elements would gradually accumulate helium. R. J. Strutt[7] has examined a large num-

[1] Proc. Phil. Soc., Camb., **14**, I. 15 (1907).
[2] *Ibid.*, **14** II. (1907).
[3] Phys. Z., Apr. 15, 1908.
[4] Phil. Mag., Sept., 1908.
[5] Compt. Rend., **149**, 30–32 (1909).
[6] THIS JOURNAL, **42**, 147 (1909).
[7] P. Roy. Soc., A, **80**, 572.

ber of minerals and finds that the amount of helium can be accounted for by the radium, uranium and thorium present (beryl being the only exception). The ratio of helium to uranium oxide present should be about 10 if the helium originates from uranium and its products. The following results indicate how closely the ratio approaches 10:

| Mineral. | Helium present in cubic mm. per kilogram. | Helium ratio. |
|---|---|---|
| Samarskite | 1,500,000 | 14 |
| Haematite | 700 | 9 |
| Galena | 2 | 17 |
| Quartz | 2 | 10 |

Another argument against the radioactivity of the ordinary elements is the temperature gradient of the earth. The amount of radium in the rocks is more than sufficient to maintain the lower strata of the earth's crust at their present temperature and if the ordinary elements were active, the temperature gradient should be much greater than it is.

Strutt was not able to prove the presence of either argon or neon in the minerals which he examined. According to Cameron and Ramsay's results these gases would be more likely to accumulate in the rocks than helium.

Several potassium minerals gave very large values for the helium ratio, thus indicating that helium may be given off slowly by potassium:

| Mineral. | Helium in cubic mm. per 100 grams. | Cc. helium per gram $U_3O_8$. |
|---|---|---|
| Rock salt | 0.223 | 3.3 |
| Sylvine (KCl) | 0.55 | 256.0 |
| Carnallite ($KMgCl_3.6H_2O$) | 0.15 | 47.0 |
| Kieserite ($MgSO_4.H_2O$) | 0.018 | 0.28 |

Strutt[1] finds that phosphatic nodules and phosphatized bones of all geological ages possess marked radioactivity, many times higher than that of rocks. This activity is due to products of the uranium series. Helium occurs in these phosphatic materials even when they are not of more than pliocene age. Large values of the helium ratio are not found for the recent deposits but are common for the older ones. Using Rutherford's values, the annual production of helium per gram of the oxide $Ur_3O_8$ is 9.13 (10)$^{-8}$ cc. By determin-

[1] P. Roy. Soc., A, **81**, 272.

ing the helium content we can estimate the age of the mineral. Strutt gives the following:

| | |
|---|---|
| Phosphatic nodules of the Crag | 225,000 years |
| Phosphatic nodules, Upper Greensand | 3,080,000 years |
| Phosphatic nodules, Lower Greensand | 3,950,000 years |
| Haematite overlying carboniferous limestone | 141,000,000 years |

W. W. STRONG.

## REVIEWS.

DAS ARBEITEN MIT FARBENEMPFINDLICHEN PLATTEN. Von DR. E. KÖNIG. Mit 2 Figuren und 16 instruktiven Tafeln. Berlin: Verlag von Gustav Schmidt. 1909. S. 75. Preis, geh., M. 2.25; geb., M. 2.85.

The majority of books on this subject contain so many formulas for the treatment of photographic plates that the reader is bewildered and at a loss where to begin in his experimental work. This fault cannot be found with the present treatment, which is condensed to 75 pages, and brings the subject down to date. Everything useless has been omitted and the treatment is very clear, especially of the subject of the effects of mixing dyes for the preparation of spectrum plates, and the consequent reduction of absolute sensitiveness for given regions of the spectrum. The book should prove very useful to every photographer who has advanced far enough to use color screens and orthochromatic plates.

R. W. W.

JAHRBUCH DER ELEKTROCHEMIE UND ANGEWANDTEN PHYSIKALISCHEN CHEMIE. Berichte über die Fortschritte des Jahres 1905. Unter Mitwirkung der HERREN DR. P. ASKENASY, Karlsruhe i. B.; DR. P. BERL, Zürich; PROF. DR. K. ELBS, Giessen; DR. F. HARMS, Würzburg; DIREKTOR J. HESS, Lechbruck; PROF. DR. H. LEY, Leipzig; DR. J. MEYER, München; DR. M. ROLOFF, Hagen; DR. O. SACKUR, Breslau. Herausgegeben von DR. PHIL. HEINRICH DANNEEL, Friedrichshagen. XII Jahrgang. Halle a. S.: Verlag von Wilhelm Knapp. 1909. pp. 1049. Price, M. 30.

This well-known "Jahrbuch," which has been of such service in electrochemistry, has acquired enormous proportions. It is divided into scientific electrochemistry and applied electrochemistry, and the scientific portion alone covers 653 pages. The book really covers a much wider field than is usually included under its title, but this is not undesirable.

A criticism that might fairly be offered of the work is that it is so far behind the literature of the subject. We desire referata that are not four years old. It must, however, not

be forgotten that the task of preparing such a work is enormous, and we should be thankful to have such a thorough review of the whole subject even if a little later than we desire. Every scientific library, as well as every electrochemist, should own the work. H. C. J.

ON THE CALCULATION OF THERMOCHEMICAL CONSTANTS. By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S. London: Edward Arnold. 1909. pp. 102.

This little work deals with the thermochemical constants of the hydrocarbons and of organic halogen, oxygen, sulphur and nitrogen compounds. A section is devoted to the thermochemical evidence for Baeyer's strain theory. This work is in convenient form for reference when any of the above-named constants is desired. H. C. J.

LES DENSITÉS DES SOLUTIONS SUCRÉES À DIFFÉRENTES TEMPÉRATURES. Calculées par D. SIDERSKY, Ingenieur-Chimiste. Paris: H. Dunod et E. Pinat. Brunswick: Friedr. Vieweg et Fils. 1908. pp. 48. Price, Fr. 3.50.

These tables, which are preceded by an introductory statement in French and German, are designed for use in sugar laboratories where it is desired to determine quickly the "apparent purity" of sugar solutions from their specific gravities. They are arranged in two groups: (1) Densities from 0.99567 (water at 30° C.) to 1.01885 (5° Brix at 15° C.) for every degree Centigrade from 10° to 30°, with corresponding sugar contents to hundredths of one per cent. Densities are given as referred to water both at 4° and at 15°. (2) Densities from 1.0188 to 1.1286 (30° Brix at 15° C.) for 10°, 15°, 20°, 25° and 30°, with sugar contents in weight and volume per cents. The tables are clearly printed and conveniently arranged and should prove well adapted to the use for which they are intended. C. A. R.

HISTOIRE DU DÉVELOPPEMENT DE LA CHIMIE DEPUIS LAVOISIER JUSQU'À NOS JOURS. Par A. LADENBURG, Professeur à l'Université de Breslau. Traduit sur la 4e édition allemande par A. CORVISY, Professeur Agrégé des Sciences Physiques au Lycée Gay-Lussac, Professeur Suppléant à l'École de Médecine et de Pharmacie de Limoges. Paris: Librairie Scientifique A. Hermann et Fils. 1909. pp. xi + 388. Price, Fr. 15.

The fourth edition of Professor Ladenburg's "Entwickelungsgeschichte," of which the present book is a translation, was reviewed in THIS JOURNAL in 1907.[1] Professor Corvisy's translation is very good indeed and the printers have done

[1] Vol. **37**, p. 656.

their part well also. It is rather surprising, however, that a book of such permanent value, no matter in what language published, should not be printed on better paper.

C. A. R.

EINFÜHRUNG IN DIE ALLGEMEINE UND ANORGANISCHE CHEMIE AUF ELEMENTARER GRUNDLAGE. Von DR. ALEXANDER SMITH, Professor der Chemie und Direktor des Institutes für allgemeine und physikalische Chemie an der Universität Chicago. Unter Mitwirkung des Verfassers übersetzt und bearbeitet von DR. ERNST STERN, Assistent am Königl. Materialprüfungsamt zu Gross-Lichterfelde-West. Mit einem Vorwort von DR. FRITZ HABER, ord. Professor an der Technischen Hochschule zu Karlsruhe. Karlsruhe i. B.: G. Braunsche Hofbuchdruckerei und Verlag. 1909. pp. xvi + 677.

The following words from Professor Haber's introduction bring out most happily what is perhaps the best feature of Professor Smith's well-known book, *viz.*, the judicious blending of the newer physical-chemical ideas with the older established method of treatment of elementary chemistry: "There are three standpoints from which we can view the broad domains of chemical science and find our way through the multitude of facts which it presents: the comparison of the elements based on the Mendeléeff system; the qualitative representation of the reactions of substances by means of structural formulas; and the quantitative treatment of phenomena on physical-chemical principles. A well-balanced familiarity with the three points of view is an incomparable advantage. The value of a training which will give this balanced knowledge is comparable to that education which gives to young people, to make their way through life, a simultaneous command over several languages. As is well known, during the years when the mind is developing, one language is learned with the other so that both are mastered with equal ease and certainty, while the matured mind which has developed complete facility of expression in one language only familiarizes itself with a foreign language only with difficulty. The use of a single point of view in our science in teaching beginners is as alluring to the academic teacher as to the student. But the more enthusiastically and emphatically this one-sided point of view is taught, the more difficult does the learner afterwards find it to adjust himself to other conceptions when, in the continuation of his studies, they are presented to him, and as the result of such training, we may easily have physical chemists without any sense of constitution or structure, or organic chemists without the physical-chemical insight. This lack of clear understanding easily becomes the source of mutual depreciation and while each group looks upon that side which

it represents as the only important one, all fail to recognize that there is but one chemistry and that the different points of view are all equally fruitful and therefore equally justifiable. Books for beginners in the study of the science which bring out the physical-chemical as well as the structural-chemical side and are based on the Mendeléeff system seem to me, therefore, to furnish the best introduction. In Smith's book, the intent of the author to make the reader familiar with the three general points of view is unmistakable."

In the present translation the English original has been closely followed in the description of experimentally established facts, but in view of the differences in the preparatory training of German and American students the theoretical portions have been considerably revised. The paper and typography are up to the German text-book standard of excellence. C. A. R.

THE CHEMISTRY AND LITERATURE OF BERYLLIUM. By CHARLES LATHROP PARSONS, B.S., Professor of Inorganic Chemistry in New Hampshire College. Easton, Pa.: The Chemical Publishing Company; London: Williams and Norgate. pp. iv + 180. Price, $2.00.

Coming from the pen of such an authority on beryllium as Professor Parsons, this book will be found, by every one interested in that element, to be a most valuable, complete and reliable source of information. The history, properties and methods of preparation of the metal and all its known normal, acid and double salts and its basic compounds are given. Says the author: "Especially is it desired to call attention to the fact that a large proportion of its accredited compounds are in reality but indefinite solid solutions. This condition of the literature of beryllium is due to the abnormal extent to which its hydroxide is soluble in solutions of its normal salts, giving rise to solids of almost any degree of basicity or to solutions with decreased osmotic effects. Accordingly, results of analysis, freezing points, etc., give little evidence of the true nature of its compounds, unless accompanied by proved definiteness of composition, a proof too often omitted throughout the whole field of inorganic chemistry, but nowhere more than in studying beryllium and its compounds."

A bibliography is appended, arranged chronologically and extending from 1798 to 1908. Up to 1902, practically all original articles and abstracts are referred to; from 1902 on, only original articles and chief abstracts. Brief abstracts of each article are included. C. A. R.

LABORATORY NOTES ON INDUSTRIAL WATER ANALYSIS. A Survey Course for Engineers. By ELLEN H. RICHARDS, Instructor in Sanitary Chemistry, Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1908. pp. iii + 49. Price, 50 cents.

This little book contains directions for carrying out a few special tests by which the engineer may decide whether any given supply of water is or is not suited for the general purposes for which it is intended to be used, *e. g.*, tests for hardness, excess of carbon dioxide, nitrates, amount of scale-forming material, iron, sulphates, alkalinity, magnesium, action on metals, oxygen consumed, oxygen dissolved, a few "remedies" for defects found, together with tables of hardness, etc., and a brief bibliography. C. A. R.